groundwater TREATMENT technology

third edition

ARCADIS
Infrastructure, environment, buildings

edited by EVAN K. NYER

Groundwater Treatment Technology

Third Edition

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Preface

"The cleanup of groundwater is unique." I first wrote those words in 1985 in the first edition of this book. Today, the words are still true. We do not clean up any other type of water (rivers, lakes, oceans, etc.). We simply stop putting contaminants in the water and allow the body of water to clean itself. However, with groundwater that self-cleaning process does not happen quickly, so we find ourselves actually cleaning the body of water as the main purpose of remediation.

While the basics of groundwater treatment have remained the same since 1985, the actual cleanup of groundwater has changed dramatically. When this book was first published, the primary method of cleaning groundwater was to move the groundwater aboveground and remove the contaminants in an aboveground treatment system. By the time the second edition was published in 1992, in situ treatment methods were becoming an important part of the remediation design. Now, in 2008 when this book was being written, in situ methods are the most prevalent way to remediate groundwater.

The second edition of this book responded to the change in remediation techniques by adding a chapter on in situ remediation and altering the remainder of the chapters to include in situ ideas in the technical discussions. Many other books have been published concentrating primarily on in situ methods with only a brief mention of aboveground treatment methods. The fact is that the remediation field has moved away from the main subject of this book, aboveground treatment design methods.

Why do a third edition then? The answer is simple. Aboveground treatment equipment is still a very important part of our treatment alternatives, and no other book available provides the reader with the unique design criteria and the detailed knowledge of these specific treatment methods. So, for this third edition, I decided to eliminate the in situ methods and make this purely an aboveground treatment publication. How the various aboveground technologies interact with in situ methods is still discussed, but the design discussion is limited to aboveground techniques.

Another factor in my decision to revisit the original subject is the increased use of aboveground treatment methods in treating emerging compounds. In the several decades since the publication of the first edition, several new organic and inorganic compounds have been identified and deemed hazardous. Many of these compounds are very soluble and are not degradable by natural bacteria. The final chapter is dedicated to these new compounds. Also, new research has prompted setting the remediation goals of several existing compounds to lower levels.

Another major change to this edition of the book is that I needed more help. Entire chapters were turned over to younger authors, who are part of a great group of engineers being mentored at ARCADIS. These young engineers have detailed knowledge about and experience with the equipment discussed in this edition of the book. So, in a departure from earlier editions, which are my personal experiences, I have tried to give these young engineers a voice. Following is a list of the authors and their chapters, as well as those people who assisted with them:

Chapter 1 Evan Nyer
Chapter 2 Gus Suarez
  - Vinay Nair
  - Antonio Cardoso

Chapter 3 Jon Forbort
  - Ally Wong

Chapter 4 Tim Terwilliger
Chapter 5 Jim Bedessem
  - Christopher Spooner

Chapter 6 Joe Darby
Chapter 7 Jon Forbort
  - Wesley May
  - Ally Wong

Chapter 8 Barry Molnaa
  - Trent Henderson

It has been my great pleasure over the years to be part of the senior staff at ARCADIS who have developed this great group of young engineers. I want to thank each one of them for their hard work in getting this book prepared. I also want to thank ARCADIS for having an aggressive policy that encourages our staff to participate in book writing. Even with the participation of all of these people, the process of creating this third edition was still a very time-consuming effort, but I think the reader will agree that the combined effort of this group has produced a very useful text.

I also would like to thank the people who provided general assistance. Christopher Spooner has been my organizational arm for this effort. Without his assistance, we would never have gotten to the end. I thank Peter Palmer for being my main backup for reviewing the chapters. Pete has applied his 30 years of experience to help make these chapters accurate, readable, and relevant to today's groundwater requirements. Finally, I thank Karen Bernhard, who provided the final review and editing for the chapters.

Groundwater remediation is still a very challenging field. Pump-and-treat systems are some of the most difficult to design because of the changes occurring in the influent conditions over the life of the project. The other authors and I hope the reader finds this text even more useful than the second edition.

1

Life Cycle Design

Evan K. Nyer
ARCADIS, Tampa, FL

In most types of water treatment, we address only the source of contamination. The main goal of wastewater treatment is to stop or limit the amount of waste entering the body of water, e.g., river, lake, or ocean. After we stop putting the pollution into the water, the body of water actually cleans itself. With drinking water or any water we would use for industrial purposes, we treat the water to remove the material not compatible with its final use. Our focus is on the condition of the water. However, groundwater treatment is unique. With groundwater treatment, we are cleaning the body of water. As with other water treatment processes, we must first remove all sources of contamination. Then, we must continue to remediate the body of water, groundwater. The groundwater actually does clean itself after the sources of contamination are removed. We just find that the natural rate of tens to thousands of years is a bit too slow.

Aquifers are also unique bodies of water. The other bodies of water that we have cleaned have been relatively easy to access and mix and are in contact with the atmosphere. Groundwater is confined, in relatively plug flow condition, and is very difficult to access. To make things more complicated, groundwater flow is not evenly distributed. Some areas flow faster than others, but all areas of the aquifer can be contaminated. All of these unique aspects of the aquifer combine to create unique requirements for remediation. If the accessibility issue can be addressed, the next design problem is that the conditions of the aquifer will change during the cleanup process. This means that the cleanup design may change over time, particularly for pump-and-treat systems, leaving the design engineer with the challenge of designing a system that has to handle changing parameters over the life of the project. We refer to this design method as *life cycle design*, and all groundwater treatment systems will have to be designed based on life cycle parameters.

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The next dilemma that we encounter with groundwater remediation is the basic choice of trying to remove the contaminants from the groundwater or to treat them in place, or in situ. There are two primary means for removing contaminants from groundwater: either air or water can be used as carriers. In both cases, we need to move the air or water past the area of contamination, trying to transfer the contaminants to the carrier. The carrier can then bring the contaminants aboveground where we pass them through a treatment system for destruction or removal. The main purpose of this book is to discuss the treatment equipment that is used when we bring the contaminants aboveground. The other major method of groundwater treatment treats the contaminants in situ. We can do this by natural chemical and biochemical reactions, enhanced natural reactions, and physical/chemical destruction or immobilization methods. This book will also quickly cover the equipment needed for delivery of the required reactants or enhancement agents with in situ remediation designs (see Chapter 4). A major limitation with groundwater treatment using carriers is that water and air are not efficient methods for removing all of the contaminants from an aquifer. For geological and hydrogeological reasons we discuss later in the chapter, water and air have a difficult time removing the last portion of the contaminants from the aquifer. This means that a pump-and-treat system does a fine job in the beginning of the project but cannot finish the cleanup in a reasonable amount of time. While aboveground treatment systems are restricted by these limitations, we have still found many situations that require air and water be used as part of our groundwater remediations. To make efficient and economic use of our aboveground treatment equipment, we must use life cycle techniques to maintain a viable treatment system over the entire life of the project.

DEFINING THE TREATMENT SYSTEM

The first thing we must do before we can select specific treatment methods is to define what we expect the aboveground treatment system to accomplish. We do this by summarizing the mass balance across the treatment system. We must understand what goes into the treatment system (the influent) and what the effluent requirements are before we can choose the best technology to accomplish the required removals. Let us start by thinking of our treatment system as a black box, Figure 1-1.

Some of the obvious parameters needed for the design of groundwater remediation systems are (1) flow, (2) influent concentrations, and

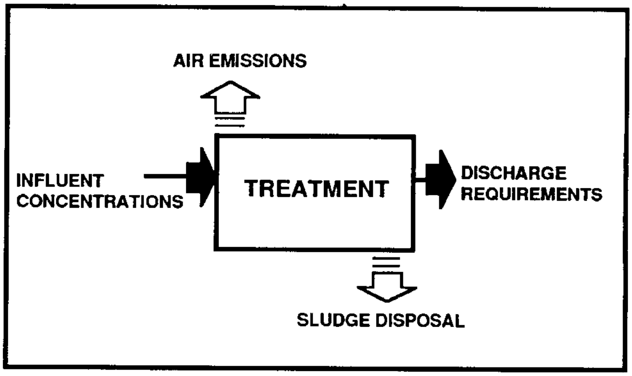

FIGURE 1-1. Parameters for defining a treatment system.

(3) discharge requirements. After we have selected the actual treatment technology, we must add other possible components to complete our mass balance around the treatment system. For example, air strippers would have air emissions, and heavy metal precipitation treatment methods would produce waste sludge. To complete our technology and cost evaluation, we must include a complete mass balance around the treatment system. A lot of the techniques that we use for groundwater treatment equipment were originally developed for municipal and industrial wastewater treatment. While this equipment is still very cost effective for groundwater treatment, we must understand and develop design specifications for use as aboveground treatment equipment. The following sections show how design parameters differ from wastewater treatment specifications and how to develop the data required for a groundwater treatment design.

Private Flow

In determining the parameters that will define the treatment technique and final system design, a good place to start is flow. In water and wastewater treatment, flow is a relatively simple parameter to determine. For municipal wastewater systems, the engineer selects a design date in the future. Most municipal systems are designed for twenty years into the future. The engineer uses population estimates to determine time, which is multiplied by a standard factor for per capita water use. To this calculation, he adds flows from industrial waste in the city and, depending on the age of the sewer system, a flow factor for rain inflow and storm sewers.

Industrial wastewater flow is determined by adding up the expected flows from each of the unit operations at the plant. Once again, depending on the age of the plant, a factor is added for storm-water runoff. In both cases, a safety factor is added, about 20 percent, to the final figure. For all of these cases, flow is not a design variable; it is a set parameter that must be determined by the engineer.

With groundwater, there are two main conditions to setting flow. Under the one condition, the main objective of the groundwater pumping system is to collect a set amount of water. This scenario is used when we are trying to stop a plume from moving past a set location (capture), or when we have a set requirement for a specific amount of water (municipal drinking water). The second condition is when we are trying to use pumping as part of our cleanup of the aquifer. With the cleanup of groundwater, flow is a design variable. The engineer does not add up the different parts of the total flow. Instead, he must weigh the effect of flow on the total cost of the system and on the time that is needed for a final cleanup. The theory is that we can increase the flow of water across the contaminated area of the aquifer and speed up the capture and removal of the contaminants. The higher flow reduces the amount of time needed to reach cleanup, but the added flow increases the size and cost of the treatment system. Let us look at the different factors that determine flow for a groundwater treatment system.

Groundwater systems have many variables that impact flow and must be considered when designing a remediation system. These variables include the type of soil or rock (aquifer) through which the water must pass, the ability of the water to pass through the soil or rock (hydraulic conductivity), the type of contamination traveling through the ground, and the hydraulic gradient of the design area.

Subsurface contaminant flow has two components, a vertical component and a horizontal component. The contaminant travels through the unsaturated zone (no water present), and encounters the aquifer. Under most conditions, groundwater is constantly moving, although this movement is usually slow, typically less than a couple of hundred feet per year. To determine flow and direction in an aquifer, basic information is needed. After we collect or estimate that basic information, groundwater flow rate may be calculated. The relationship for flow is stated in Darcy's law, where

$$Q = -KA\,dh/dl$$

where

Q = groundwater flow rate
A = cross-sectional area of flow
dh/dl = hydraulic gradient: hydraulic head loss measured between two points (wells) in the direction of groundwater flow divided by the distance between the two points
K = hydraulic conductivity, a measure of the ability of the porous media to transmit water.

To determine the direction and amount of flow, three or more wells may be drilled into the aquifer and the heads or water levels measured and compared to a datum (typically mean sea level). Groundwater will flow from high head to low head (the negative sign in Darcy's law is for direction). The hydraulic conductivity (K) is a function of the porous medium (aquifer); finer-grained sediments such as silts and clays have relatively low values of K, whereas sand and gravel will have higher values. Other physical factors, such as porosity, packing, and sorting, may affect the hydraulic conductivity. The chemistry of the groundwater and the contamination may also affect K by causing contaminants to adhere to clay particles or by causing constituent precipitation (such as iron), both of which may reduce the permeability. As can be seen in Figure 1-2, the contamination plume almost always travels in the direction of the groundwater flow.

To move groundwater up to the treatment system, a vertical or horizontal well or trench may be constructed penetrating the aquifer. A pump is used to move the contaminated water to the surface. As was discussed earlier, the head differences measured in the aquifer determine groundwater flow. As we remove water from the aquifer by pumping, water levels and head relationships change. It can be seen by adding only one or two pumping wells to a groundwater remediation system that the overall groundwater flow patterns become very complicated. This is one reason why we need the assistance of hydrogeologists when designing a groundwater remediation system. Drawdown around a pumping well is called the zone of influence (see Figure 1-3). The success of many groundwater remediation systems is dependent on defining and understanding the dynamics of the zone of influence and the area surrounding a pumping well.

Proper well placement and design in the appropriate hydrogeologic unit may stop and reverse the contamination plume. The pump will

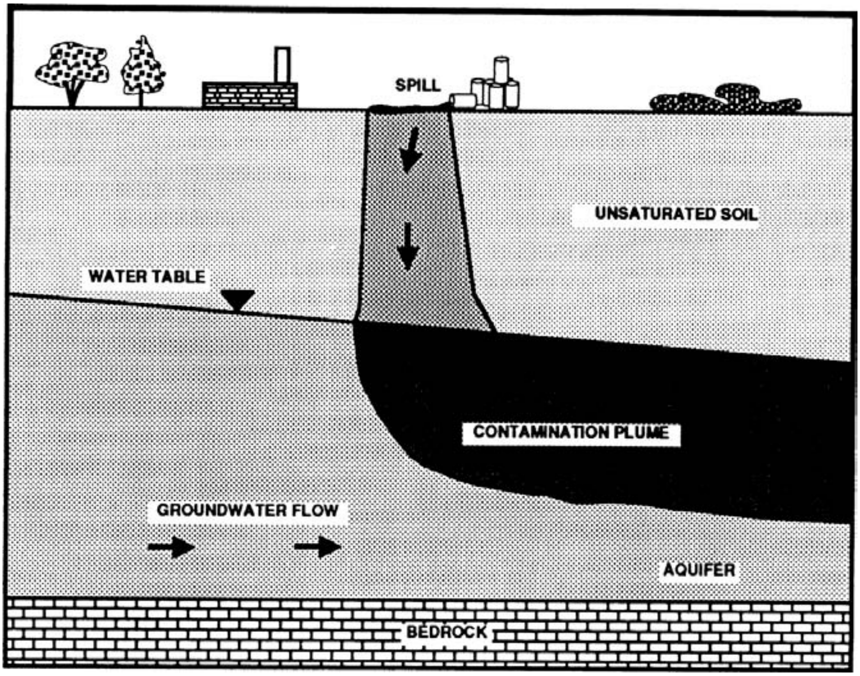

FIGURE 1-2. Contamination plume in an aquifer.

extract contaminated groundwater from the well and transport it by conveyance pipelines to the aboveground treatment system. The first factor in the groundwater recovery system design is the flow necessary to stop and/or reverse the movement of the contamination plume.

Other methods that may be used to control the movement of the plume include the installation of hydraulic and physical barriers. Hydraulic barriers typically consist of numerous injection wells placed to alter the groundwater flow patterns. The hydraulic barriers may be placed downgradient of the contamination or at other strategic locations to enhance the effectiveness of a groundwater recovery system. One of the great disadvantages of hydraulic barriers is that they may require a significant amount of clean water. Installation of injection wells may be limited by local, state, and federal permitting authorities or the actual physical properties of the soil or rock. Oftentimes, the treated groundwater effluent is used to form the hydraulic barrier.

Physical barriers, such as clay slurry walls, sheet piles, and grout curtains, can be placed upgradient or downgradient of the

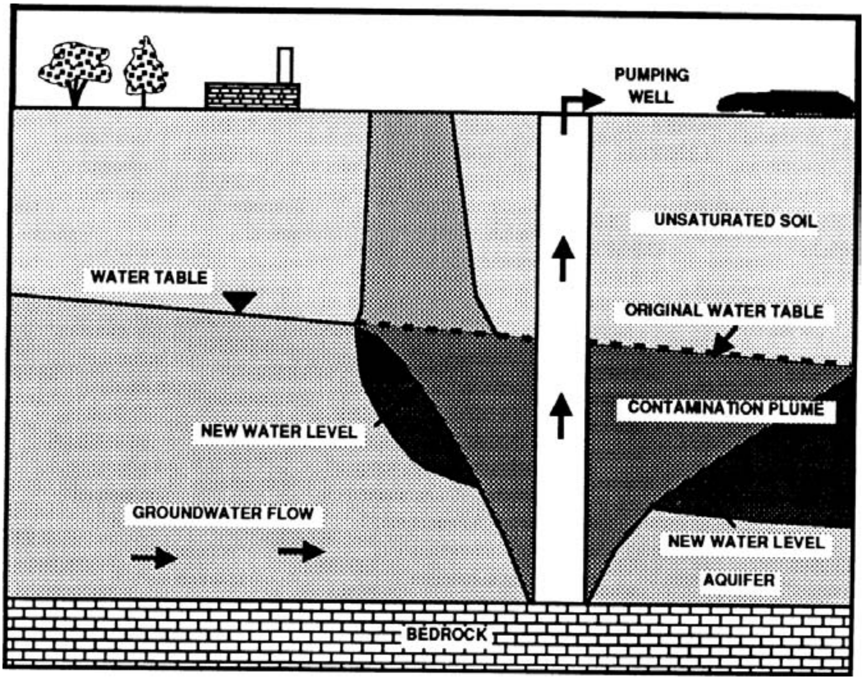

FIGURE 1-3. Zone of influence from a pumping well.

contamination or completely surrounding the contamination plume. When correctly designed and constructed, a physical barrier can isolate the contamination from the groundwater flow system. Eliminating groundwater movement through the contaminated zone can control plume expansion.

Defining the physical setting for the subsurface barriers is necessary for ensuring their overall effectiveness. Project oversight by hydrogeologists, engineers familiar with underground structures, and geotechnical engineers is needed to determine the applicability of physical barriers. Barrier use may be severely limited by site characteristics and cost. These physical barriers must be keyed into confining layers to limit the (horizontal/vertical) movement of contaminants; the deeper the significant confining layer, the higher the construction cost. At depths greater than 60 to 100 feet, constructing a physical barrier of sufficient integrity is difficult and may require the installation of an extensive monitoring system to review the barrier's effectiveness. Site characteristics alone may preclude the use of subsurface barriers. Regardless, the cost of their installation must be compared to the cost of stopping the plume movement by groundwater recovery. Even under ideal conditions, physical barriers will not be perfect and only slow the movement of the contaminant. On a practical level, if you think of physical barriers as a bank vault that will lock in the contaminant, you will be disappointed.

The aquifer depicted in Figure 1-2 and Figure 1-3 is the "ideal" aquifer. In many cases, the geologic units below the base of the aquifer have permeabilities high enough to allow the interchange of groundwater between the aquifer and the units below. Also, the thickness of the aquifer could be extensive, and a plume may not reach the aquifer base. It is beyond the scope of this book to discuss the many groundwater and aquifer systems. The basic idea is that the contamination plume needs to be stopped and that one of the factors for controlling the plume is groundwater flow from a recovery well or trench system. All of the design factors discussed in this chapter are discussed in basic terms. The "treatment design engineer" will always have to work with staff who are knowledgeable about the subsurface hydraulics. The reverse is also true. The final cleanup design should not solely rest with the hydrogeologists. The two disciplines must work together to develop the most cost-effective remedial alternative.

The second factor that may have to be considered as part of flow is the amount of water entering the contamination area on a local or regional scale. One part of this has already been discussed. Slurry walls, or similar barrier walls, can interrupt the flow into or out of the contamination site. Two other possible entry points into the contaminated site are recharge of surface water from streams and lakes and recharge from rain that can percolate down to the aquifer. In addition, the bedrock and other sediments below the aquifer may provide a source of groundwater by upward leakage. This is rare but has to be considered, especially while pumping water from the upper aquifer.

Water from the surface can be controlled by either capping the contamination site with an impermeable layer or by providing good surface area drainage directed away from the site. Water coming from below is much harder to control and will probably have to be added to the flow for the treatment system.

The third factor in flow to the treatment system is the length of time in which the cleanup is to occur. In most groundwater systems, the more water that is pumped from the well, the lower the level of water surrounding the well. This will increase the head differential in the groundwater and force the water at a faster rate to the well. There is a limit to how fast water can travel through an aquifer, and it is very easy in many aquifers to pump a well dry. The relationship between pumping rate, system design, and the time necessary to remediate a site is often complicated. The engineer or project manager must decide between the cost of increasing the size of the treatment system and the savings by reducing the time for groundwater cleanup.

The relationship between system flow and cleanup time is complicated. When assessing any groundwater contamination site, it is necessary to identify the source or sources of contamination. The second step is to stop those sources from contributing to the already expanding contamination plume. Sources of contamination may be an underground storage tank, a surface source, or even residual contamination or product within the saturated and/or unsaturated portion of the subsurface. For example, Figure 1-2 shows the contaminants flowing through the unsaturated zone to the aquifer. Let us assume that a well is placed within the contamination plume and that maximum flow over a period of three months is sufficient to completely eliminate the plume. The equipment is packed up, and everyone leaves. A problem could arise if the source has not been identified and stopped; there are still contaminants in the unsaturated zone. These contaminants may still migrate to the aquifer, and three months later another contamination plume could form.

One solution to this problem is that the original cleanup must be slowed so that the natural flushing methods have a chance to bring most of the contaminants through the unsaturated zone. Of course, an alternative would be to speed up the natural flushing action and maintain the original speed of the cleanup, or to combine a groundwater method with a vadose zone treatment method such as vapor extraction to treat both areas at the same time.

Another example, one that cannot be solved as readily, is seasonal variation in the groundwater level. As one would expect, during times of high rainfall, the overall level in the aquifer can increase. The problem arises when the level recedes, and the contaminants are left behind in the unsaturated zone. The next time that the groundwater level is high or rain percolates through the ground, the contaminants will reenter the aquifer. In these cases, the best solution may be to slow down the flow to the treatment system and perform the cleanup over several high-water seasons; to excavate and remove the contaminated soil; or, once again, to apply a vadose zone treatment method at the same.

Other factors will have a relatively minor effect on flow to the treatment system. The number of recovery wells or trenches used will have an effect on the amount of flow for cleanup. The effectiveness of wells and trenches to pull in the contamination and to remediate the site is dependent on the location of the recovery system. Systems located on the edges of the plume may be successful in capturing contaminants located there but need to be designed to minimize the amount of clean water collected from outside the plume. Successful recovery system locations also have to take into account "nonflow" zones caused by the design of the system. Nonflow or dead zones may be successfully captured by alternating the pumping schedule by sequencing pumps on and off. Although the idea is to clean up the groundwater, many other factors may come into play when selecting recovery system locations. For instance, a second recovery system located near the center of the contamination may also be required. The larger the plume, the more likely we will need a second or multiple recovery system(s) to capture the entire plume. Another example is setting the recovery system inside the plume, capturing most of the plume and allowing the leading edge of the plume to naturally attenuate. This example is most prominent when the pumping system is set up at the edge of the owner's property. The pumping system ensures that no more contaminants will leave the property and the material that has left the property is low enough in concentration for natural attenuation methods to eliminate the rest of the plume.

Discharge requirements need to be considered in designing the flow rate to an aboveground treatment system. More flow will be required if some of the water is to be used to flush the unsaturated zone of contamination. Water returned to the site can decrease the time for cleanup by increasing the hydraulic head and forcing groundwater to the central recovery point at a faster rate. This may be limited by the hydraulic properties of the soils above the groundwater. This same water will increase the total water entering the site, and the flow to the treatment system will increase accordingly. The effect of discharge requirements is discussed further in the text.

In summary, hydraulic properties of the aquifer and soils above the aquifer will control groundwater flow to the treatment system. The following factors have to be considered when determining flow to the groundwater treatment system:

- Stop/reverse movement of the contamination plume
- Amount of water entering the contamination site on a local level
- The rate at which the cleanup is to occur
- The recovery system to be used
- The final disposal/use of the treated water

LIFE CYCLE FLOW CONSIDERATIONS

The amount of water discharged from the treatment system will probably remain the same during the life of the project. The amount of water that is being reused on-site may vary during the cleanup. This would include when the water is being used to increase the hydraulic head at the end of the plume, to flush contaminants from the unsaturated zone, or for in situ treatment. For these three cases, the flow to the treatment system may change during the project. Water may be reused to increase the hydraulic head and remediate the plume in cases when the end of the plume is relatively far from the central well or wells or in cases when additional time for cleanup is not available, Figure 1-4.

Near the end of the remediation period, the plume will shrink to its original contamination site. There will no longer be any reason to reuse treated water to help move the plume. However, injection water may still be used to speed the progress of the project.

The same thing may happen when water is being reused to flush the contaminants from the unsaturated zone, Figure 1-5. Near the end of the project, the contaminants will have been flushed, and only aquifer cleanup may be necessary.

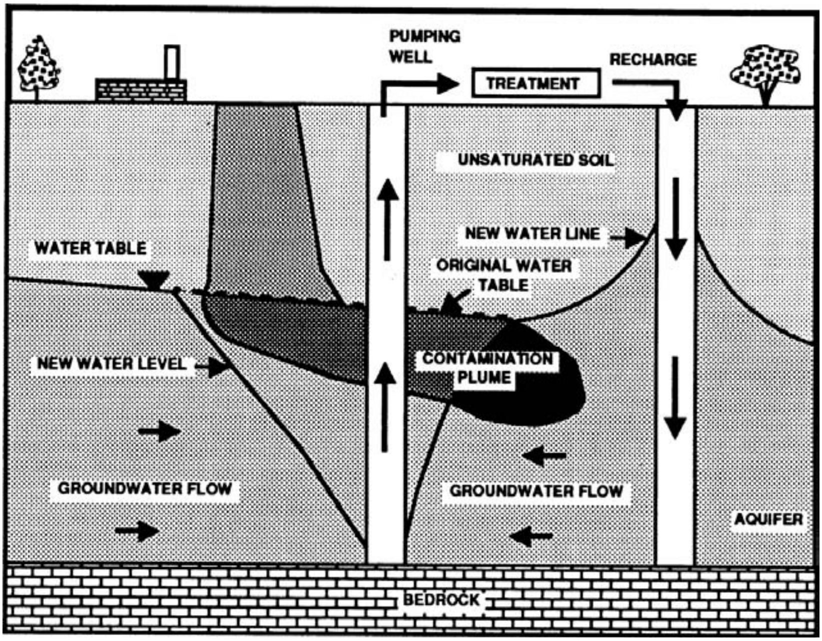

FIGURE 1-4. Effect of a recharge well on groundwater flow patterns.

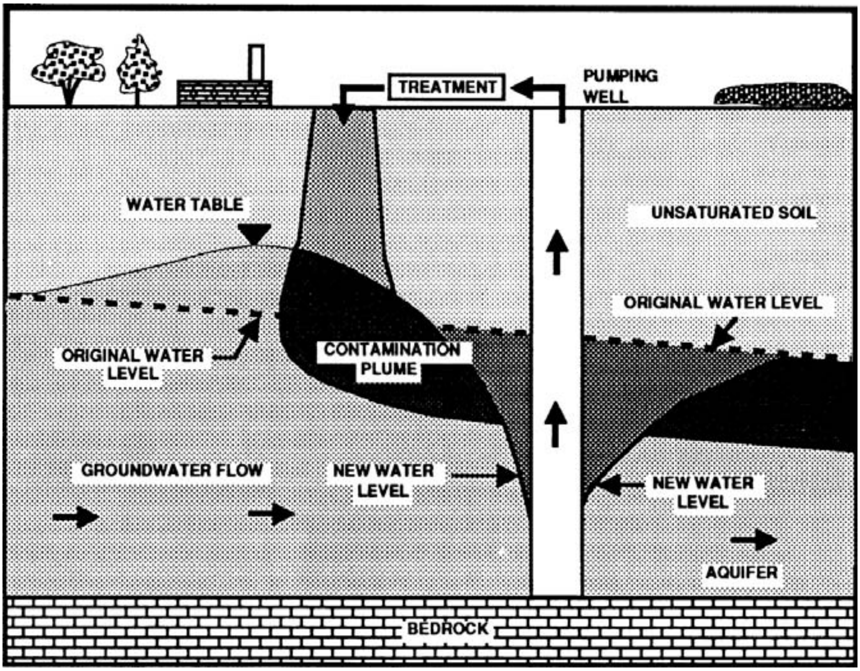

FIGURE 1-5. Effect of a surface recharge on groundwater flow patterns.

At this point, the engineer may decide to eliminate the reuse of groundwater. This is also the case for in situ treatment. At the end of the project, the concentration of contaminants in the aquifer may be low enough to discontinue the recirculation of water. As in all good water treatment designs, provisions must be made for flow fluctuation. In addition to these major flow considerations discussed, other factors can affect the flow during the life of the project. Two main factors in groundwater treatment are drought and loss of power.

There are natural fluctuations in the level of groundwater during the year. Most designs are based on the maximum water that the aquifer can transfer. However, during low-water situations, as in droughts, water flow may be limited. The design should have provisions for low flow rates.

Power loss or any mechanical difficulty that stops flow to the treatment system must be figured into the system's design. These problems are especially troublesome during winter operation but can affect the maintenance of the system at any time of the year. We discuss shutdown periods, planned and unplanned, in Chapter 7.

INFLUENT CONCENTRATION

The concentrations of contaminants in groundwater are normally determined by sampling the water from a well. The types of contaminants will depend on the material originally lost to the ground. The relative concentration will depend on where the well intersects the contamination plume. The farther away from the original spill site, the more dilution, dispersion, and contaminant degradation will occur to the original contamination plume. Several wells will have to be constructed to get a full picture of the plume (and the hydrogeology). The hydrogeologist may provide insight and guidance in the selection of wells for the monitoring system.

In addition to the distance from the spill site, several other factors affect the concentration of the contaminants. These factors include the amount of contaminant reaching the aquifer, solubility and density, groundwater flow rate, distance to the water table, and time. These factors will all affect the size of the treatment system and the length of time that the system must be operated for a completed project.

The amount of contaminant reaching the aquifer is made up of several components. The first is the amount of contaminant lost to the ground. The first question to ask is whether the source of contamination has been eliminated. In certain cases the contamination is still being introduced into the ground. An example of this is a landfill. Other cases also exist and may include hydrocarbons trapped in the unsaturated zone beneath a gas station. Leachate generation is also an example of a continual contaminant source. Leachate is generated when water flow through the contaminated zone causes a continual addition of new contamination to the groundwater (subsurface).

When the source of contamination is defined and stopped, the hydrogeologist may assist in attempting to determine the total amount of material lost to the ground. Not all of the material lost to the ground will reach the aquifer. The unsaturated zone above the aquifer will adsorb a percentage of the contaminants. It is widely reported that only 50 percent of the gasoline in a spill from a storage tank normally reaches the aquifer. Of course, this amount depends on the type of soil in the unsaturated zone, the distance to the aquifer, and the total amount of material spilled.

The next component of contaminant concentration in the aquifer comes from the solubility and the density of the material spilled. A large portion of the materials spilled into the ground may not be soluble in water. When a material not soluble in water reaches the aquifer, it does not mix. Figure 1-6 depicts a gasoline spill.

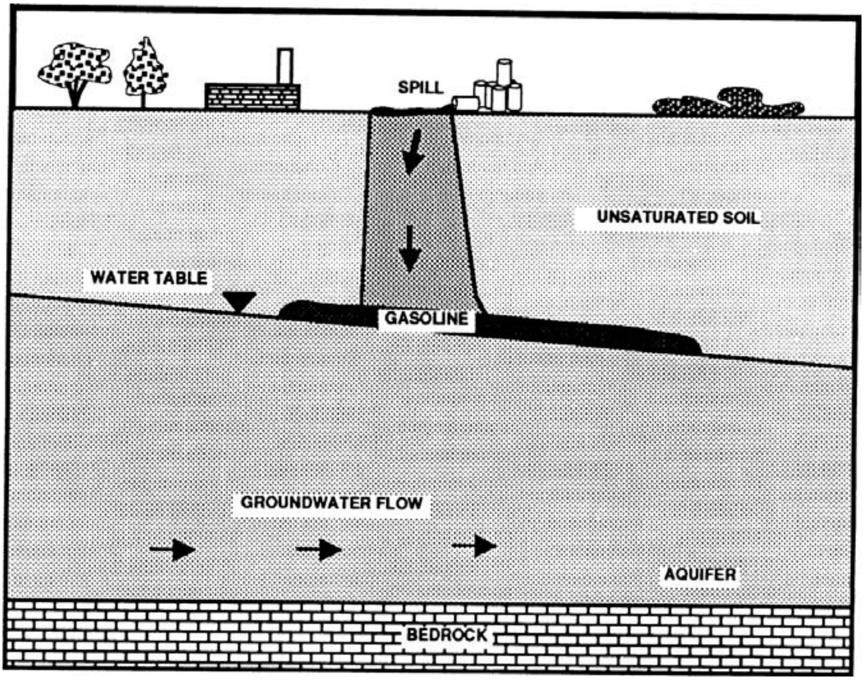

FIGURE 1-6. Gasoline spill encountering an aquifer.

The main component of the gasoline does not enter the aquifer. It floats atop the aquifer and spreads in all directions. A small percentage of the gasoline, mainly benzene, toluene, ethylbenzene, and xylenes (collectively BTEX) compounds, typically found in unleaded gasoline, does enter the aquifer and may form the normal plume. Modern mixtures of gasoline may also include ethyl alcohol and/or methyl tertiary butyl ether (MTBE). Both of these compounds are very soluble. Gasoline is lighter than water, so it normally floats atop the aquifer. Compounds with this characteristic are referred to as light nonaqueous phase liquids (LNAPLs). Most straight-chain hydrocarbons are lighter than water and will stay atop the aquifer. Compounds that are heavier than water usually sink to the bottom of the aquifer and are referred to as dense nonaqueous phase liquids (DNAPLs). Trichloroethene is a DNAPL, and Figure 1-7 depicts how a DNAPL like trichloroethene moves through an aquifer as a result of a spill.

Table 1-1 lists the specific gravity of 40 compounds. This list, combined with the solubility of the compound, Table 1-2, will assist the groundwater scientist in determining where to find a particular compound after it is spilled into the ground. The section on Pure

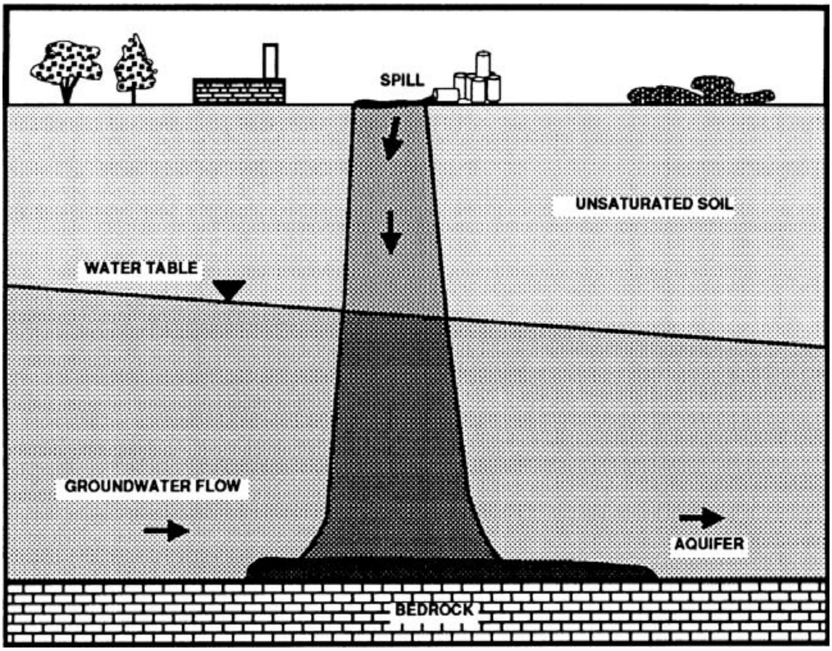

FIGURE 1-7. Trichloroethene spill passing through an aquifer.

Compound Recovery in Chapter 2 discusses locating and removing these compounds from the subsurface.

The amount of water flow through the aquifer will also have an affect on the contaminant concentration in the aquifer. The more water that passes the original spill site, the more dilution or dispersion will occur. Once again, the groundwater scientist must decide on the economics of limiting groundwater flow with a physical structure or hydraulic controls. Finally, these components combine to form a time effect on contaminant concentrations. There are three patterns that contaminant concentrations follow over the life of the project. These patterns are summarized in Figure 1-8.

First, there is the constant concentration exhibited by a leachate. If we do not remove the source of contamination, then the source will replace the contaminants as fast as the groundwater system can remove them. Until the source of contamination is remediated, the concentration will remain the same. We normally think of “mine” leachate or “landfill” leachate. But, anytime there is a continual source of contamination, we are dealing with a leachate.

The second possible pattern is when the contamination plume is being drawn toward the groundwater removal system. This mainly

TABLE 1-1 Specific Gravity for Specific Organic Compounds

	Compound	Specific Gravity*	Reference
1	Acetone	.791	1
2	Benzene	.879	1
3	Bromodichloromethane	2.006 (15°C/4°)	1
4	Bromoform	2.903 (15°C)	1
5	Carbon tetrachloride	1.594	1
6	Chlorobenzene	1.106	1
7	Chloroform	1.49 (20°C liquid)	2
8	2-Chlorophenol	1.241 (18.2°C/15°C)	1
9	p-Dichlorobenzene (1,4)	1.458 (21°C)	1
10	1,1-Dichloroethane	1.176	1
11	1,2-Dichloroethane	1.253	1
12	1,1-Dichloroethylene	1.250 (15°C)	1
13	cis-1,2-Dichloroethylene	1.27 (25°C liquid)	2
14	trans-1,2-Dichloroethylene	1.27 (25°C liquid)	2
15	Ethylbenzene	.867	1
16	Hexachlorobenzene	2.044	1
17	Methylene chloride	1.366	1
18	Methylethylketone	.805	1
19	Methyl naphthalene	1.025 (14°C/4°C)	1
20	Methyl tert-butyl-ether	.731	1
21	Naphthalene	1.145	1
22	Pentachlorophenol	1.978 (22°C)	1
23	Phenol	1.071 (25°C/4°C)	1
24	Tetrachloroethylene	1.631 (15°C/4°C)	1
25	Toluene	.866	1
26	1,1,1-Trichloroethane	1.346 (15°C/4°C)	1
27	1,1,2-Trichloroethane	1.441 (25.5°C/4°C)	1
28	Trichloroethylene	1.466 (20°C/20°C)	1
29	Vinyl chloride	.908 (25°C/25°C)	1
30	o-Xylene	.880	1

*Specific gravity measured for the compound at 20°C referred to water at 4°C unless specified otherwise (20°C/4°C).

1. *Lange's Handbook of Chemistry*, 11th edition, by John A. Dean, McGraw-Hill Book Co., New York, 1973.
2. *Hazardous Chemicals Data Book*, 2nd edition, by G. Weiss, Noyes Data Corp., New York, 1986.

happens with municipal drinking water. In this situation, the concentration increases over time. The well is originally clean but becomes more contaminated as the plume is drawn toward the well. There are several specific requirements when dealing with water that is going to be used for drinking water.

The final pattern is associated with remediation. In this case, if the original source of contamination is removed, the concentration of the contaminants decreases over time. This is mainly the result of mass removal but is also due to retardation, natural chemical and biochemical reactions, and dilution from the surrounding groundwater.

TABLE 1-2 Solubility for Specific Organic Compounds

	Compound	Solubility (mg/l)	Reference
1	Acetone	$1 \times 10^{6*}$	1
2	Benzene	1.75×10^3	1(A)
3	Bromodichloromethane	4.4×10^3	2
4	Bromoform	3.01×10^3	1(B)
5	Carbon tetrachloride	7.57×10^2	1(A)
6	Chlorobenzene	4.66×10^2	1(A)
7	Chloroform	8.2×10^3	1(A)
8	2-Chlorophenol	2.9×10^4	2
9	p-Dichlorobenzene (1,4)	7.9×10^1	2
10	1,1-Dichloroethane	5.5×10^3	1(A)
11	1,2-Dichloroethane	8.52×10^3	1(A)
12	1,1-Dichloroethylene	2.25×10^3	1(A)
13	cis-1,2-Dichloroethylene	3.5×10^3	1(A)
14	trans-1,2-Dichloroethylene	6.3×10^3	1(A)
15	Ethylbenzene	1.52×10^2	1(A)
16	Hexachlorobenzene	6×10^{-3}	1(A)
17	Methylene chloride	2×10^4	1(B)
18	Methylethylketone	2.68×10^5	1(A)
19	Methyl naphthalene	2.54×10^1	2
20	Methyl tert-butyl-ether	4.8	3
21	Naphthalene	3.2×10^1	2
22	Pentachlorophenol	1.4×10^1	1(B)
23	Phenol	9.3×10^4	1(A)
24	Tetrachloroethylene	1.5×10^2	1(A)
25	Toluene	5.35×10^2	1(A)
26	1,1,1-Trichloroethane	1.5×10^3	1(A)
27	1,1,2-Trichloroethane	4.5×10^3	1(A)
28	Trichloroethylene	1.1×10^3	1(A)
29	Vinyl chloride	2.67×10^3	1(A)
30	o-Xylene	1.75×10^2	1(C)

*Solubility of 1,000,000 mg/l assigned because of reported “infinite solubility” in the literature.

1. *Superfund Public Health Evaluation Manual*, Office of Emergency and Remedial Response Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, 1986.
   A. Environmental Criteria and Assessment Office (ECAO), EPA, *Health Effects Assessments for Specific Chemicals*, 1985.
   B. Mabey, W. R., Smith, J. H., Rodoll, R. T., Johnson, H. L., Mill, T., Chou, T. W., Gates, J., Patridge, I. W., Jaber H., and Vanderberg, D., *Aquatic Fate Process Data for Organic Priority Pollutants*, EPA Contract Nos. 68-01-3867 and 68-03-2981 by SRI International, for Monitoring and Data Support Division, Office of Water Regulations and Standards, Washington, D.C., 1982.
   C. Dawson, et al., *Physical/Chemical Properties of Hazardous Waste Constituents*, by Southeast Environmental Research Laboratory for USEPA, 1980.
2. USEPA *Basics of Pump-and-Treat Ground-Water Remediation Technology*, EPA/600/8-901003, Robert S. Kerr Environmental Research Laboratory, March 1990.
3. Manufacturer’s data; Texas Petrochemicals Corporation, *Gasoline Grade Methyl tertbutyl ether Shipping Specification and Technical Data*, 1986.

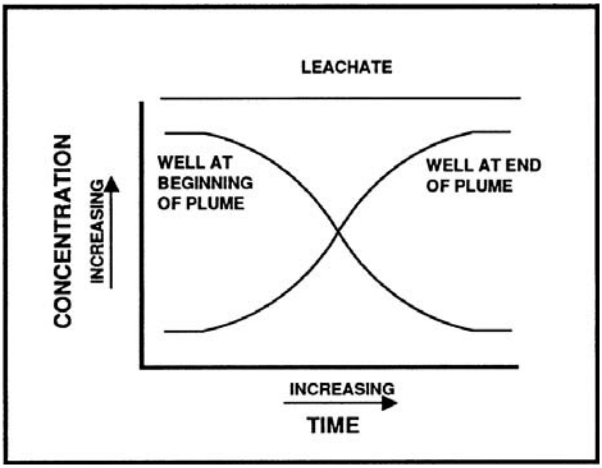

FIGURE 1-8. Time effect on concentration found in a well.

Concentration data may be collected by drilling wells and by sampling the groundwater in the wells. The separate data from the wells can be combined in different ways. One can average all of the data, use a weighted average reflecting the influence of specific wells, or just take the maximum concentration found in all of the wells. The weighted average is probably the most accurate method, and the hydrogeologist may assist by providing the weighting criteria. The maximum concentration is the least accurate method, but it is sometimes used. The logic is that if the treatment system can handle the highest concentration, it will have no problems with the lower concentrations. This method is also used for wastewater. But, it is a dangerous design method for groundwater. Several treatment methods will have a catastrophic failure if the concentration goes below a minimum (biological and heavy metal removal are two examples). Other treatment methods will not be optimized based on maximum concentration.

Accurate concentrations are required for the proper design of treatment systems. The authors' experiences have shown that the weighted average (the more accurate the weight factors, the more accurate the final concentration) is the best method to use. Even with accurate concentration data, flow estimates, and weighting factors, most designs overestimate the concentrations entering the treatment system. The problem is that we want to make sure that the treatment system will successfully remove all of the contaminants, so we err on the side of caution. The important thing is to make sure that the treatment system can treat the highest expected concentration and be flexible enough to treat lower concentrations. Flexibility is the key to a successful groundwater treatment system design.

LIFE CYCLE CONCENTRATION CONSIDERATIONS

Figure 1-9 illustrates the decline of concentration over time.

The design engineer cannot assume that the lower the concentration, the better the treatment system will operate. Certain processes are designed based on a minimum concentration. These units will lose efficiency with lower concentrations and not function at all when a minimum concentration is reached. The design engineer must also take into account that the operational costs may be reduced as the concentration decreases. In either case, the design must be able to accommodate the entire life cycle concentration of the project. Three examples of the effect of concentration on system unit operations follow.

Treatment methods for organic contaminants are discussed in Chapters 2 and 3, and treatment methods for inorganic contaminants are discussed in Chapter 5. The reader should refer to those three chapters for details on the following examples. First, let us look at the effect of time on an organic contaminant that we will treat with biological methods, specifically using the activated sludge method. Assume Figure 1-10 represents the influent life cycle concentration.

The concentrations are provided as total organic carbon (TOC). We will assume that the organic carbon in the groundwater is degradable and that the TOC to biochemical oxygen demand (BOD) is one to one.

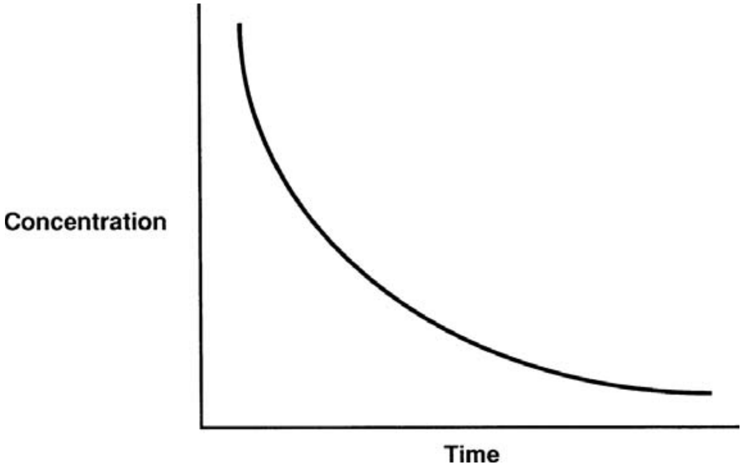

FIGURE 1-9. Life cycle concentration of a remediation project.

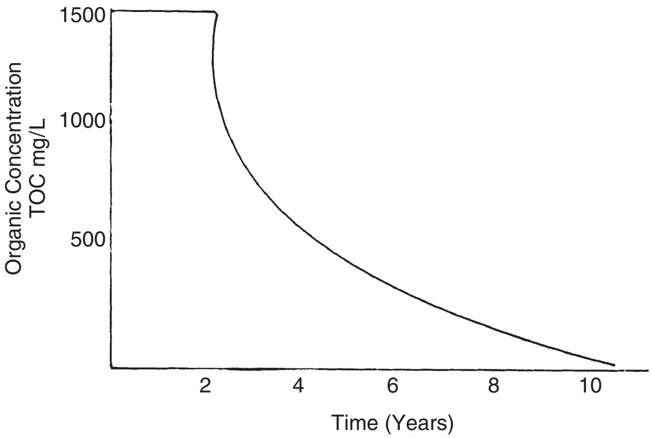

FIGURE 1-10. Life cycle concentration from a well at the center of the plume for an organic contaminant.

The flow (*Q*) will be 25,000 gallons per day (gal/day) for the entire life of the project. Also assume that all other environmental parameters are acceptable for biological treatment. (The authors realize the activated sludge process is not widely used for groundwater treatment. The main purpose of this example is to show the possible effect that change in concentration has on the operation of any treatment system. Activated sludge still has its place among possible treatment technologies for groundwater.) Figure 1-11 illustrates the proposed treatment system.

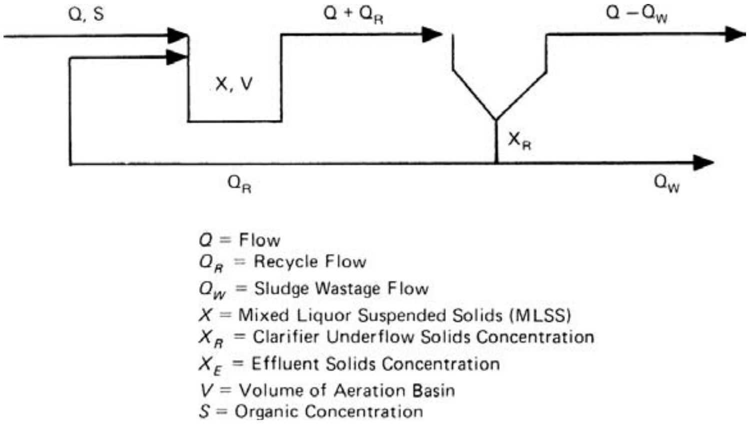

FIGURE 1-11. Activated sludge treatment system.

As is discussed in Chapter 3 the activated sludge process depends on the settling properties of the growing bacteria. To keep the bacteria in a growth phase in which they settle properly, the bacteria should have a sludge age (*A*) between 5 and 20 days. Let us look at what happens to the sludge age during the life of the project.

Assume:

Mixed liquor suspended solids (MLSS) (X) = 3,000 milligrams per liter (mg/L)

Yield coefficient (Y) = 0.25 pound bacteria per pound organic

Volume of the aeration tank (V) = 40,000 gallons

$A = (X^*V)/(Q^*S^*Y)$

For year 1, S = 1,500 mg/L, A = 12.8 days

For year 3, S = 1,200 mg/L, A = 16 days

For year 5, S = 600 mg/L, A = 32 days

For year 7, S = 300 mg/L, A = 64 days

As can be seen from these data, the system will maintain the proper sludge age for about 4 years. After that time, the sludge age will be too high, the bacteria will lose their settling properties, and the clarifier will not be able to separate the bacteria from the treated water. When the clarifier fails, the system will not be able to maintain a high concentration of bacteria in the aeration basin. At that point, the system will no longer remove a high percentage of the incoming organic contaminants.

One solution to this problem is to lower the MLSS concentration. Figure 1-12 summarizes the sludge ages for the treatment system at an MLSS level of 3,000 mg/L and 1,500 mg/L.

This does extend the useful life of the treatment system, but the system still fails before the cleanup can be completed. And there is a lower limit to the MLSS. The MLSS concentration entering the clarifier must be around 1,250 mg/L or above to ensure proper settling. Bacteria rely on flocculation to settle. A critical mass is required to ensure enough contact between the flocculating particles.

Another method to extend the useful life of the system is to divide the aeration basin into two or more tanks. In our example, we could use two 20,000-gallon tanks instead of the one 40,000-gallon tank.

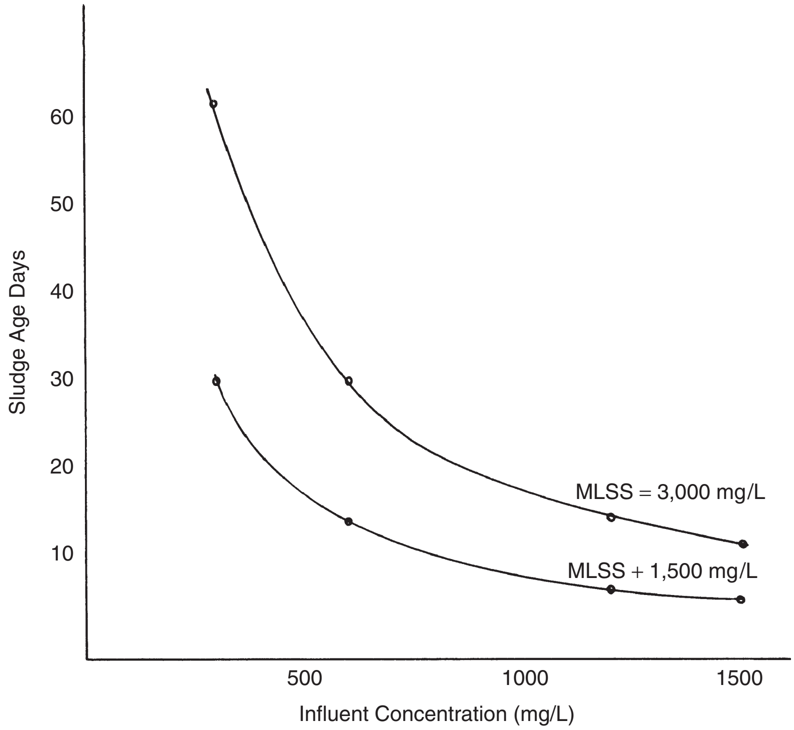

FIGURE 1-12. Sludge age with life cycle influent concentrations.

Assuming 1,500 mg/L MLSS, at year 6, one aeration basin could be shut down. This would effectively half the sludge age in the system at a steady MLSS. An added advantage of this method would be that half of the blowers could also be shut down. The system not only would last longer but would also cost less to run in the final years of operation.

Of course, there are limitations to an activated sludge system designed this way. The final few years of the cleanup will still create a very long sludge age. The actual design may need to include different unit operations so groundwater cleanup can continue throughout the entire life cycle. The point is that the change in concentration of contaminants over the life of the project may have a detrimental effect on the performance of the treatment system. The design engineer must take into account the entire range of concentrations when designing the treatment system.

Similar limitations will affect fixed-film, biological treatment system designs. These problems are not limited to biological systems;

inorganic treatment systems also have life cycle considerations. For our second example, let us consider an aquifer contaminated with a heavy metal.

The design details for removing a heavy metal from water are covered in Chapter 5. For this example, assume that by adding lime, to a pH of 9, all of the heavy metal comes out of solution as metal hydroxides. Suspended solids that must be separated from the water are formed. Figure 1-13 summarizes the life cycle concentration for the heavy metal. Assume that laboratory analysis is performed, and Figure 1-14 summarizes the concentration of suspended solids resulting from lime precipitation of the heavy metal at various concentrations.

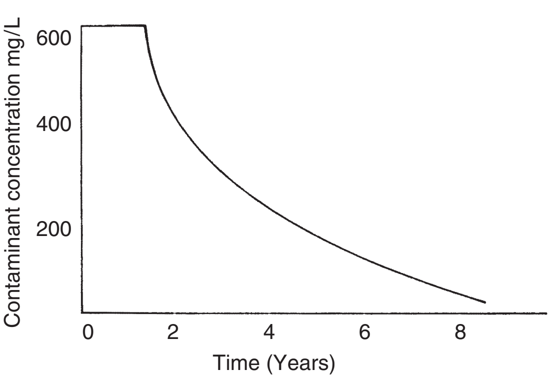

FIGURE 1-13. Life cycle concentration from a well at the center of the plume for an inorganic containment.

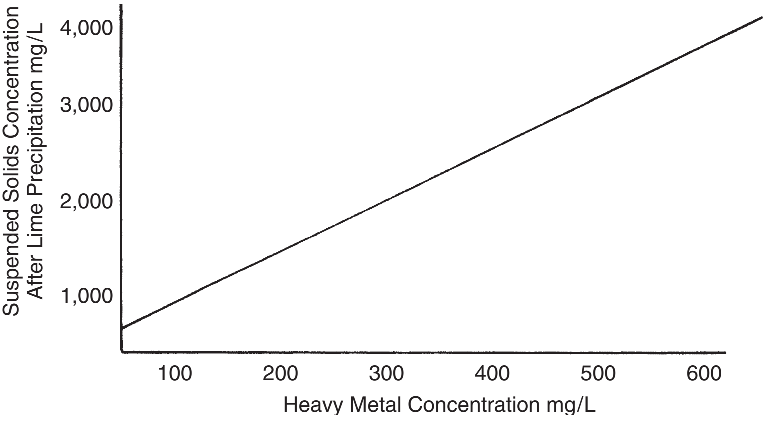

FIGURE 1-14. Suspended solids from lime precipitation of a heavy metal.

From these data, the design engineer must select the proper unit operation for separating the suspended solids from the groundwater. During the first couple of years, the concentration of suspended solids will be approximately 4,000 mg/L. In this range, the main problem with separation will be the thickening of the solids as they are removed from the water. A standard clarifier, with its design based on thickening, is the proper unit operation.

After year 3, the standard clarifier is no longer effective for solids removal. Metal hydroxide suspended solids rely on flocculation to be removed from the water. As in activated sludge, a critical mass must be present to ensure enough contacts for proper flocculation, settling, and thickening. As the suspended solids drop below 1,000 mg/L, the preferred separator would be a flocculating clarifier. As the solids decreased to less than 500 mg/L, a solids contact clarifier would be required. The flocculating clarifier has a chamber that increases the number of contacts between floc particles before entering the clarifier zone. The solids contact clarifier allows previously settled solids to contact incoming solids, giving them a critical mass for settling.

During the final years of the project, the concentration of suspended solids would be so low that a sand filter or dual-media filter would be required to remove the contaminants. The filter would be the proper selection after the suspended solids were below 100 mg/L. Finally, the heavy metal concentration would be at the point that lime precipitation would not be the proper method of treatment. When the heavy metal concentration is less than 5 mg/L, another technology, such as ion exchange, would be a more cost-effective treatment technique. (It should be noted that all of the concentration values given in this example are approximations. Every heavy metal and groundwater will react differently with lime precipitation. Only through laboratory testing can the design engineer determine when these different levels will be reached.)

Separation of the suspended solids is not the only problem the design engineer must face. Metal hydroxide sludge must be dewatered or solidified before it can be disposed of economically. Once again, the proper unit operation depends on the amount of solids to be processed. Of course, this value will change over the life of the project.

The final treatment plant design must take all the above requirements into consideration. The design engineer must try to maximize the number of years that the treatment plant will function. Figure 1-15 shows one possible design incorporating life cycle considerations. Groundwater is brought into contact with lime in a flash mix tank. The

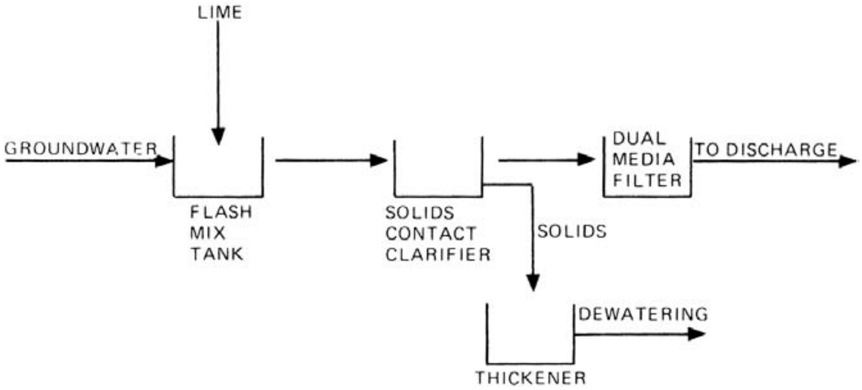

FIGURE 1-15. Life cycle treatment plant design for a heavy metal.

liquid/solids mixture is sent to a solids contact clarifier. The effluent water from the clarifier is sent to a filter, and the sludge is sent to a thickener.

The solids contact clarifier should be designed at a relatively high flow rate. The high solids loading in the beginning years can be quickly transferred to the thickener. The solids that escape because of the high loading will be captured by the filter. During the middle years, the solids contact clarifier will maintain the critical mass necessary for proper settling.

The filter should be a dual-media or continuous backwash design. These designs can handle a higher concentration of suspended solids. In the beginning years, the filter will remove the solids from the overloaded solids contact clarifier. During the final years, the clarifier can be shut down, and the filter will remove all of the suspended solids.

The thickener will handle the high load of solids during the first several years. During the middle and end years, the thickener will act as a storage tank so that the solids dewatering activities can be run on a periodic basis. The solids dewatering will have to use extra manpower and/equipment during the beginning years that will have to be scheduled during the middle and final years.

Finally, when the concentration reaches a very low level, all the equipment in Figure 1-15 will have to be shut down. An ion exchange unit will be installed and operated until the last of the heavy metals has been removed from the groundwater.

Of course, Figure 1-15 represents only one possible design. It would be impossible to list all the different designs for this treatment problem.

Local conditions may favor a different solution to this design problem. The important concept is for the design engineer to use life cycle considerations when designing the treatment plant.

These same life cycle problems will exist on other unit operations. Although for certain treatment systems, the effect will be related more to operational costs than physical design and possible failure. Carbon adsorption and air stripping fit into this category. Neither of these unit operations will fail as the concentration decreases. However, there may be significant cost savings to using other treatment technologies as the concentration decreases. The design engineer must also consider the capital and operational costs throughout the entire project when developing his design.

Our final example covers the effect on operational costs from a life cycle design. Let us compare the costs of a carbon adsorption system to a packed tower air stripper with vapor-phase carbon adsorption. The design criteria for this example will be as follows:

Flow: 40 gallons per minute (gpm)
Benzene: 1 mg/L

No other contaminants are present, and there is nothing that can interfere with the treatment processes, i.e., silt or iron. To keep the example simple, we will use previous published data.[1] If the reader would like more details on the design or costs presented here, they are available from that source.

The carbon system will consist of two 800-pound carbon units in series. We will assume that the capital cost is $4,200. The operating costs for a carbon system mainly come from the cost of replacement carbon, disposal of used carbon, and transportation of the carbon. We will assume that these costs will be $1.25 per pound, $1.75 per pound, and $1.50 per pound, respectively. The total operating cost will, therefore, be $4.50 per pound carbon. We will assume that the carbon usage rate is 8 pounds of carbon per pound of benzene. The total carbon adsorption costs will be $4,200 for capital and $17.30 per day for operating.

We will assume that the air stripper will be a 14-inch-diameter packed tower with 15 feet of packing. The capital cost will be $11,000. A blower is required for all air strippers, and the operating cost for the blower will be $0.60 per day. The treatment system will also include a vapor-phase carbon unit and a heater. The heater is required to maintain the air at below water saturation. This is necessary to obtain higher carbon efficiency in an airstream than is possible in a water stream. The total capital cost of the heater and the vapor-phase carbon unit is $7,500. We will assume that the carbon capacity is 2 pounds of carbon per pound of benzene. Vapor-phase carbon costs a little more than liquid-phase carbon. Therefore, the total carbon costs will be increased to $5.00 per pound for carbon. Finally, the heater will require 1.9 kilowatts (kW) to increase the air temperature to the required levels. The daily costs for the air blower, heater, and carbon will be $0.60, $4.50, and $4.80, respectively. The total cost for the air stripper with vapor-phase carbon is $18,500 for capital and $9.90 per day for operating. (The reader is reminded that all of these numbers are for illustration purposes only. The costs listed here are not accurate for these technologies on specific applications. The engineer must develop his/her own cost estimates for a particular site. Once again, the point of these values is to serve as an example of life cycle design considerations.)

Let us now compare these two designs by using constant influent values and by using life cycle design. Figure 1-16 shows the cumulative costs of the two systems assuming constant influent.

The carbon system has a lower capital cost but a higher operating cost. While the total costs are lower for carbon in the first few years, the lower operating cost of the air stripper with vapor-phase carbon catch up later on. The breakeven point is 4.8 years. If the remediation was going to last less than 4.8 years, then the carbon adsorption system would be favored. The air stripper with vapor-phase carbon would be

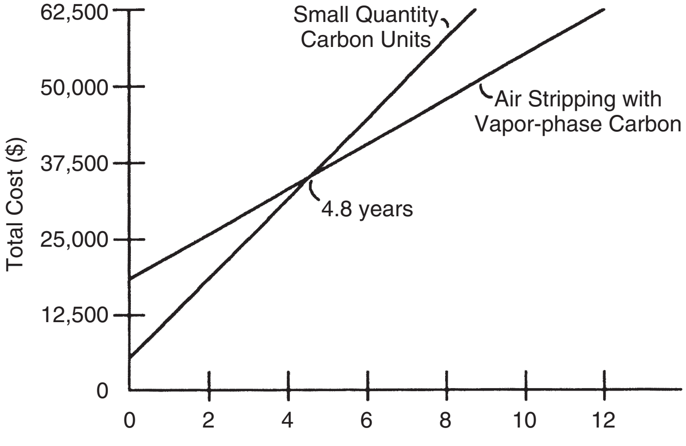

FIGURE 1-16. Cumulative costs of carbon adsorption and air stripping with vapor phase carbon.

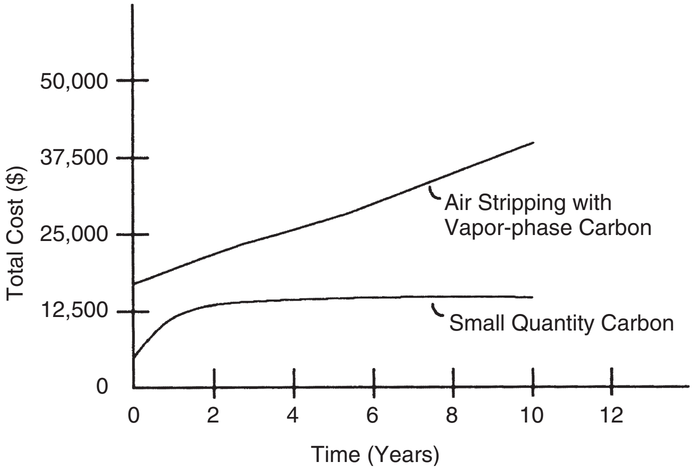

FIGURE 1-17. Life cycle design cumulative costs of carbon adsorption and air stripping with vapor phase carbon.

favored for longer projects. The comparison is very different if we use life cycle design. Let us assume that the benzene concentration decreases by 50 percent per year. At the end of year 1, the concentration is 0.5 mg/L. At the end of year 2, the concentration is 0.25 mg/L, etc. Figure 1-17 summarizes the new cumulative costs.

As can be seen, the capital costs remain the same, only the operating costs are affected—they are lower. However, the decrease in operating costs for the carbon system are so significant that the lower cost of carbon for the vapor-phase carbon system never overcomes the capital and other operating costs (i.e., the air heating costs would remain the same, even as the concentration decreases) of that system.

At a minimum, life cycle design must be used to develop accurate costs of treatment for a groundwater remediation. As can be seen in this last example, life cycle design can also affect the type of treatment used for the remediation.

There is one practical suggestion to finalize this concentration discussion: Most sites require an aquifer pumping test as part of the site studies. The aquifer pumping test can also be used as a method to gather concentration data. Concentration samples should be collected near the end of the aquifer pumping test. If there is a desire to see the immediate time effect on concentration, then use a general organic measurement (TOC; total petroleum hydrocarbons [TPH], etc.) on samples taken every half to full hour. A full analysis can be completed two to three times during the testing period.

DISHCHARGE REQUIREMENTS

The treatment plant design will also depend on the final disposition of the treated water. The engineer must decide whether the water will be discharged to a surface water body, to another treatment system, or to a direct use, or returned to the ground or aquifer. The discharge requirements for each of these cases will have a major effect on the size and complexity of the treatment system.

The discharge may be sent directly to a stream or other surface water body. Such discharges are regulated by the National Pollutant Discharge Elimination System (NPDES) program. It must be determined if the discharge will be direct or indirect (discharges to publicly owned treatment works [POTWs] are indirect), if it is a regulated categorical industry discharge, or if it requires bioassay testing prior to discharge. The following would be typical effluent requirements for a direct discharge: 10 to 30 mg/L BOD, 10 to 30 mg/L total suspended solids (TSS), 1 to 5 mg/L oil and grease, less than 1 mg/L for ammonia, 1 to 10 mg/L for nitrate, less than 1 mg/L for any heavy metal (significantly less for mercury and some other heavy metals), and between 0.001 and 0.5 mg/L for specific toxic organics. Of course, certain direct discharges have much more restrictive effluent requirements. Always check with the local regulators on specific discharge requirements. Also, some requirements have nothing to do with the contamination at your site. We had one site that forced us to test for dioxins as part of our discharge permit. Required monitoring and reporting associated with permitted discharges may add significant costs to the treatment system.

Another method for final disposal of recovered groundwater is discharge to another treatment system, either a POTW or an industrial wastewater treatment system. One of the advantages of discharging to the POTW is that the groundwater can be discharged to nearby sewer lines. The advantage of discharging to the industrial wastewater system is that the type and concentration of the contaminants can be higher than would normally be allowed for an NPDES discharge.

The contaminants will have to be compatible with the waste that is already processed by the off-site treatment system. Some pretreatment may be necessary for either type of plant. The industrial plant may require neutralization, heavy metal removal, or pure compound removal. The POTW will usually require that the water entering the sewer not exceed the normal concentration of domestic waste. The following would be typical limits for discharges to a POTW: 250 mg/L BOD, 250 mg/L TSS, 100 mg/L oil and grease, less than 1 mg/L for any heavy metal, and between 0.5 and 5 mg/L for specific toxic organics. Total water flow can also be a problem for a POTW. Some plants are near their capacities and cannot accept any more water flow into the plant. Regulations for each treatment plant will be different, and the potential plant will have to be contacted and discharge limitations established. Local ordinances also govern discharges to POTWs. It is also far-sighted to review the POTW's compliance history with its NPDES permits. It is not recommended to discharge to a POTW that may be under review for significant noncompliance.

There can be significant costs associated with discharge to a POTW. Some POTWs have a policy of charging a connection fee in addition to the daily charges based on flow. Also, any compound above the regulated concentration can be subject to a surcharge. All of these fees add up, and a direct discharge is usually less expensive for large flow systems. Engineers should make sure to get a complete fee schedule to include in their cost analysis when considering discharge to a POTW.

In an increasing number of situations, spills have affected a drinking water source or other final use source. To reuse the treated groundwater in these cases requires treatment to stringent effluent discharge requirements. It should be noted in these cases that contaminant concentrations are normally very low or the well would have been abandoned. Federal drinking water standards should be reviewed to determine discharge requirements. Naturally occurring compounds may also require treatment as part of a drinking water system. Arsenic is a good example. Engineers may have to include these compounds in their treatment system design so that the discharge is acceptable to the final user. Of course, these natural compounds can add significant costs to the treatment system. Determining who should be responsible for these added costs is always interesting.

Finally, the water from the well can be returned to the ground. If the water is to be returned to the ground, the recharge system should be strategically placed to affect the movement of the plume. Figure 1-4 shows the water being returned at the end of the plume. This will increase the hydraulic head and may force the plume back to the central well.

The recharged water may also act to flush the unsaturated zone of contaminants. Figure 1-5 shows the treated water being returned at the surface where the spill originally occurred. This process can be part of an in situ treatment. In situ treatment is discussed in Chapter 4. If the water is to be used at the end of the plume, the discharge requirements will be strict. This is because not all of the water will return to the central well. Any water escaping the zone of influence should be at background aquifer concentrations.

If the water is to be used to flush the contaminants or as part of an in situ treatment, the level of treatment will be much lower. In fact, in the case of biological treatment, leaving some of the bacteria and the resultant enzymes will help solubilize, flush, and degrade the contaminants in the soil.

CAPITAL COSTS

We discussed earlier in this chapter that the total time for a cleanup would usually be less than the 20 years, as for a wastewater project. Also, we saw that even if the life of the project is ten years, probably not all of the equipment would be needed for the entire time. In this section, we discuss the effect of time on the cost of equipment.

Most of the equipment used in the field will have a 5- to 20-year life expectancy. Pumps and other equipment with moving parts have a shorter life expectancy, and tanks and reaction vessels have a longer life expectancy. The cost of equipment in wastewater treatment is figured over the life expectancy of the equipment. The cost of equipment for a groundwater cleanup must be based on the time used on the project, with an upper limitation of the life expectancy of the equipment.

Let us assume that the cost of equipment for the activated sludge treatment system example in the previous section was \$100,000. If we set the amount of time that we need the equipment and the interest rate that we have to pay for the equipment, then we can calculate the daily cost of the equipment.

One formula for calculating costs would be

$$C = \text{Cap}/\{[1 - (1 + i)^{**} - n]/i\}$$

where

C = cost per time period n
Cap = capital cost (\$100,000 in our example)
i = the interest rate
n = the period of time

We will assume that the interest rate is 8 percent. If the equipment is used for 10 years, the daily cost is \$41 per day. If the equipment is needed for only 5 years, the daily cost is \$67 per day. At 2 years, the

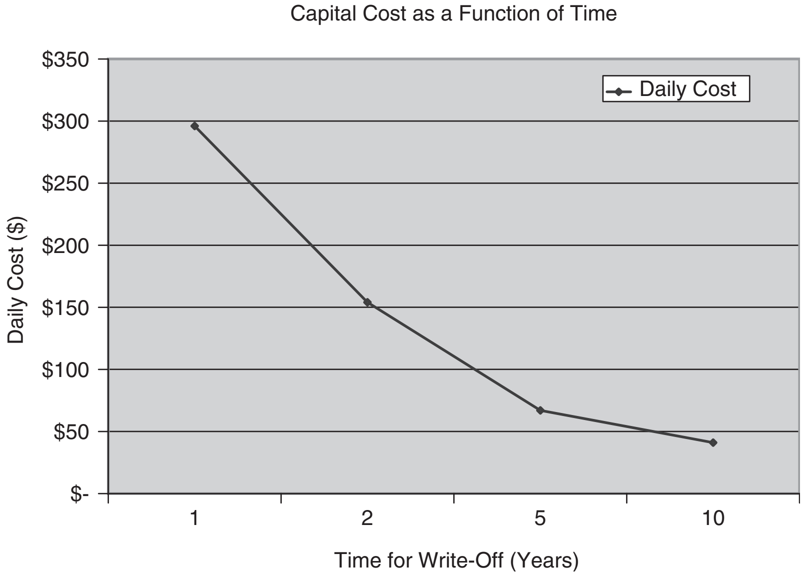

FIGURE 1-18. Capital cost as a function of time.

daily cost is $154 per day, and at 1 year, the daily cost is $296 per day. Figure 1-18 summarizes the daily cost of equipment when used for various periods of time.

As can be seen, the cost of equipment gets significantly higher as the time of use decreases. One method of comparing the cost of treatment by different technologies is to base the comparison on cost of treatment per gallon of water treated. At a flow of 25,000 gal/day, the cost of treatment goes from $0.00192 per gallon at 10 years to $0.01184 per gallon at 1 year. Using the same equipment for 1 year will cost six times as much per gallon treated as using the same equipment for 10 years.

While the water portion of the treatment systems usually lasts 5 to 20 years, some components of groundwater cleanups may be completed in a 1- to 2-year period. Any equipment associated with air as the carrier (sparging, vapor extraction, etc.) would normally be used for much shorter periods of time: 1 to 2 years. This makes the cost of equipment over time another part of the life cycle design. The design engineer will have a problem on shorter projects and on longer projects in which a particular piece of equipment is needed for only a short period of time. An obvious solution for short-term use is to rent the equipment or to use it on several different projects. This would allow the equipment to be capitalized over 10 years even though it is only required for 1 year on a particular project.

Of course, any equipment that is to be used on more than one project will have to be transported from one site to the next. The equipment will have to be portable. For example, a design engineer has a choice of one tank 17 feet in diameter or two tanks 12 feet in diameter. If the equipment is to be used only a short period of time, the appropriate choice would be the two 12-foot-diameter tanks. The legal limit for a wide load on a truck is 12 feet.

In general, to be transported by truck, treatment equipment should also be less than 10 feet in height and 60 feet in length. Rail transport can take longer units, but to be able to reach most of the United States, shipment by truck should be assumed in the design.

Since the first edition of this book was published in 1985, the authors have been able to see the effect that the concepts in this book have had on the design methods used in the field. While the life cycle design concept in general has been well accepted, the capital cost portion has been ignored. Most engineers simply add up the cost of capital and operating a treatment system with no regard to the life cycle effect on capital costs. In most cases, this is due to the difficulty in using equipment at more than one site and other practical problems with reusing equipment.

The reader should consider life cycle capital costs when performing a design analysis. Rental equipment may be available for portions of the treatment system. Less expensive equipment with a shorter life expectancy may be a good option (i.e., plastic tanks instead of steel tanks). Even if the final design is not changed, a life cycle capital costs analysis can be an important part of understanding the groundwater treatment system.

OPERATOR EXPENSES

One final area that has to be discussed under life cycle design is operator expenses. Any system that requires operator attention will cost more to operate than a system that does not require operators. All wastewater treatment system designs usually have operator expenses factored into their review. With groundwater treatment systems, this cost factor takes on added importance.

The main reason for this importance is the relative size of a groundwater treatment system. Once again, the engineer cannot just take a design developed for wastewater treatment systems and reduce its size for groundwater treatment. Most groundwater treatment systems will be very small in comparison to most wastewater treatment systems. The operator costs, therefore, become more significant.

Let us look at the biological treatment system example once again. Assume a 15-horsepower (HP) blower is required for the system at \$0.06 per kilowatt-hour (kWh). In addition, chemicals and miscellaneous costs are \$3.00 per day. At a 10-year life for the equipment, the daily costs would be as follows:

Equipment	\$48.00
Power	\$29.00
Chemicals	\$ 3.00
Total	\$80.00

Figure 1-19 summarizes the relative costs for each category. Without any operator attention, the equipment represents 60 percent of the daily cost of operation. The power is 36 percent and the chemicals are 4 percent of the daily costs. Figure 1-20 shows what happens to this relationship if one operator is required for one 8-hour shift per day and is paid, including benefits, \$10.00 per hour. Now 50 percent of the daily cost is related to operator costs. Equipment drops to 30 percent, power to 18 percent, and chemicals to 2 percent. At just one

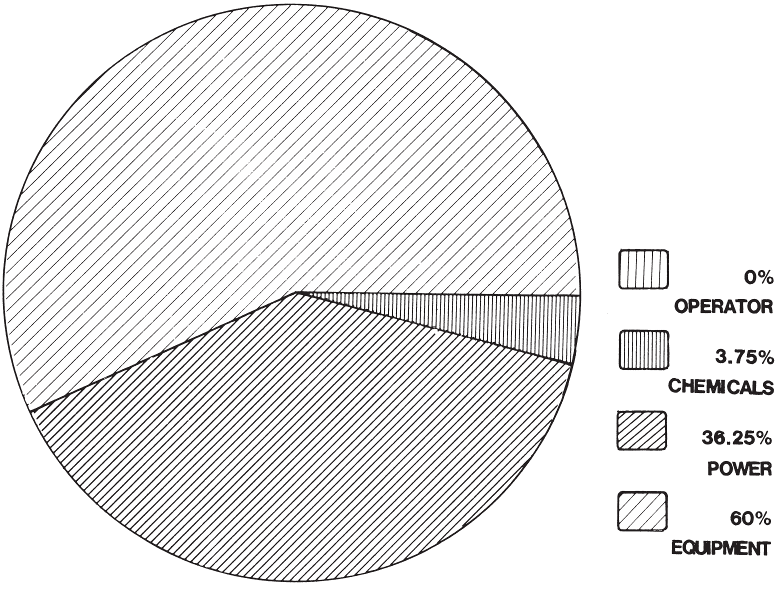

FIGURE 1-19. Ratio of daily costs with no operator attention.

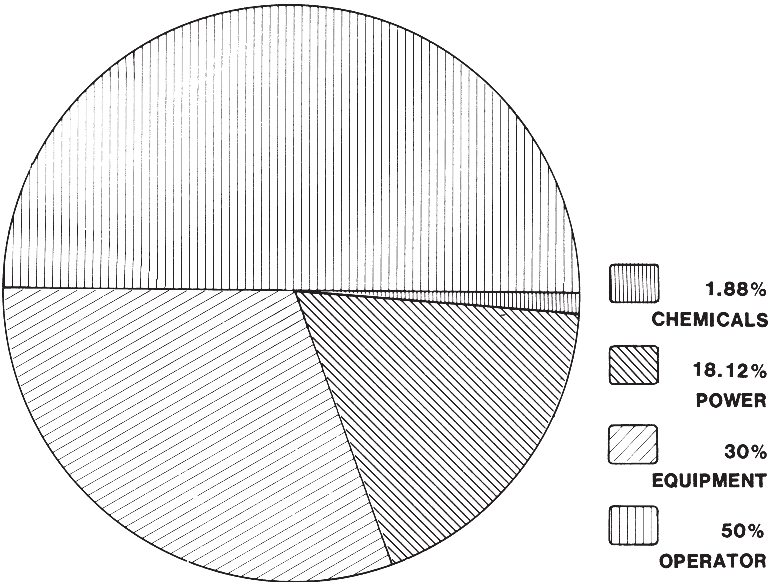

FIGURE 1-20. Ratio of daily costs with hours per day of operator attention.

shift per day, the operator is now the main expense of the treatment system.

If the treatment system requires full-time observation, the operator costs become even more important. Figure 1-21 shows the relative costs when an operator is required 24 hours per day and paid $10.00 per hour. Now, the operator represents 75 percent of the cost of operation. Three out of every four dollars spent on the project would go to personnel.

Daily costs for the project double if an operator is required for 8 hours per day compared to operating with no personnel. The costs triple at two shifts per day and quadruples when around-the-clock attention is required. These costs are summarized in Figure 1-22.

As can be seen from these data, the design engineer cannot ignore the effect of the operator on treatment system cost. In fact, the designer should spend most of his effort on minimizing the operator time required for a particular design.

The effect of the operator does not decrease significantly even as the size of the equipment increases. Figure 1-23 represents the relative costs from a treatment system five times the size of the present example and requiring 24 hours per day of operator attention. The operator still represents over one-third the cost of treatment. Even as the total cost of the treatment system approaches $500,000, the design engineer must

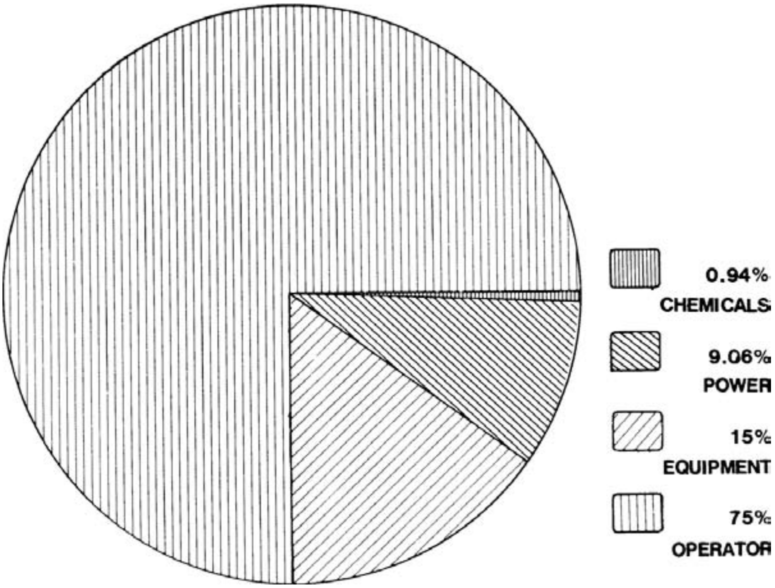

FIGURE 1-21. Ratio of daily costs with 24 hours per day of operator attention.

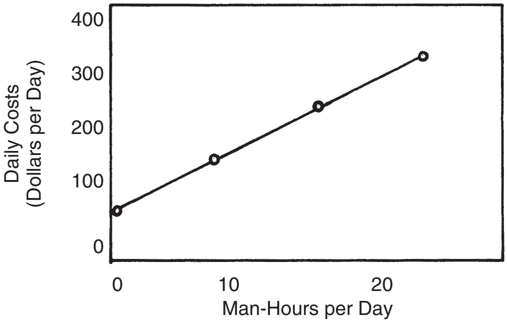

FIGURE 1-22. Daily costs of treatment with variable operator attention.

take special precaution to keep the required operator attention to a minimum.

GATHERING A COMPLETE SET OF DATA FOR THE TREATMENT DESIGN

We have now reviewed the major components needed to design a groundwater treatment system. Even with all of these data, we will not be completely certain that the design will be perfect for the

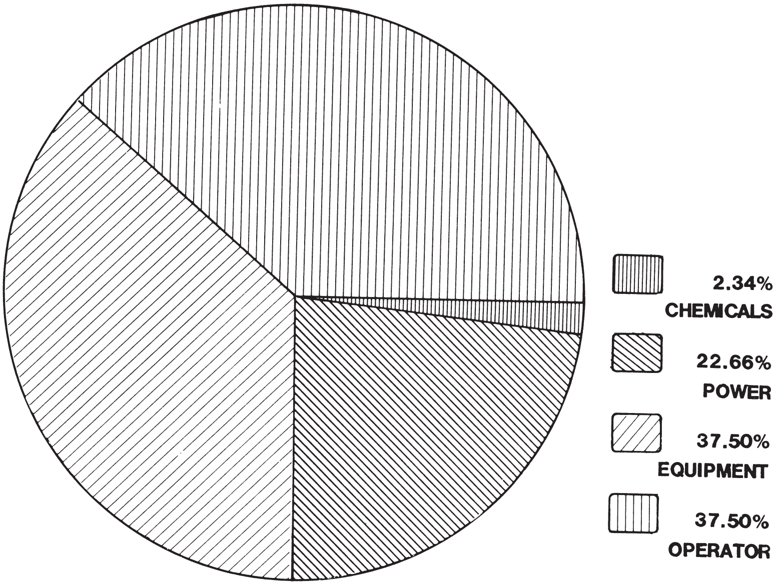

FIGURE 1-23. Ratio of daily costs for a $500,000 treatment system with 24 hours per day of operator attention.

groundwater that we pump at the start of the project. One of the continuing problems with groundwater is determining how much information is needed to accurately define the actual conditions. All we really have is numbers on a piece of paper. Do these numbers represent what the groundwater treatment system will see when it starts up? How many data points are needed to define a concentration? How many data points are needed to define a flow rate?

It is very easy to turn a site into a “pincushion” and install numerous borings and wells. It is also easy to take a multitude of samples from each well and spend millions of dollars on analysis. Even after all of this effort and money, there will still be a significant amount of uncertainty with the design data.

This is the result of the highly variable physical conditions in the subsurface. It is impossible to obtain detailed physical information on the unsaturated zone or the aquifer. Geotechnical engineers have used an “observational” design method originally developed by Karl Terzaghi and R.B. Peck to create designs for foundations, dams, etc., for many years. This method uses limited data from the site, incorporates experience from similar situations, and produces a design that can be slightly modified as the last of the data arrive during construction or start-up.

The observation method of design also has a place with the design of groundwater treatment systems. We will never be able to gather enough data to be 100 percent certain of the design. We must use a combination of data from the field and experience from similar installations. In addition, our final design for the treatment system should include the ability to adjust to further changes as we gain full understanding of the nature of the groundwater from the actual pumping.

The engineer will never know with certainty what the treatment system will receive until the pumps are turned on. And those data are good only until the life cycle changes start to take effect.

References

1. Nyer, E. K., The effect of time on treatment economics, Groundwater Monitoring Review, Spring 1989.
2. Terzaghi, Karl and Peck, R. B. Groundwater and Soil Contamination Remediation: Toward Compatible Science, Policy, and Public Perception, National Academy Press, 1990.

2

Treatment for Organic Contaminants: Physical/Chemical Methods

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When a pure organic contaminant is released onto or into the ground, the main force on the movement of the compound is gravity. If the ground is porous, the spill will move downward. There will be some lateral spread of the movement, controlled by the porosity of the soil. The speed of movement will be dependent on the viscosity of the material spilled and the porosity of the soil. Several things can happen to the contaminant as it progresses downward before it encounters the aquifer. Initially, the contaminant may undergo any of the following: adsorption on the soil particles, volatilization, biological degradation, and, usually to a lesser degree, hydrolysis, oxidation, reduction, and dehydrohalogenation.[1] Additionally, the contaminant may encounter an impermeable barrier (clay, bedrock, etc.) that may stop or alter the downward progress.

The adsorption on a soil depends on both the contaminant and the soil matrix. The solubility, octanol–water partition coefficient (K_{ow}), and molecular structure of the contaminant are important factors in determining adsorption capacity. In general, the more soluble the compound, the less it will be adsorbed to the soils. The octanol–water partition coefficient represents the distribution of a chemical between octanol and water phases in contact with each other at equilibrium conditions. The higher the octanol–water partition coefficient, the more likely it will adsorb to soils.

The molecular structure relates to the contaminant's[1] polarity and size, which directly affects adsorption. These factors are also important if the contaminant reaches the aquifer. Adsorption to soil particles will also occur in the aquifer. That is why contaminants move slower in

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an aquifer than in water. The contaminants adsorb and are retarded by the soil particles.

The amount of surface area and organic content are also important soil matrix factors that determine adsorption capacity.[1] The greater surface area associated with clays and clayey material provides more adsorption capacity. Higher organic content increases the number of potential adsorption sites and therefore increases adsorption capacity.

As the contaminant moves in the soil, each soil particle will adsorb a small amount of the material. The material adsorbed stays with the soil and no longer moves with the main flow of the contaminant. If the spill does not reach an impermeable layer or aquifer first, the spill will eventually exhaust itself in the soil and stop all primary movement.

The amount of soil required to adsorb all of the material released depends on two factors: the porosity of the soil and the absorbability of the contaminant as reflected by its characteristic *maximum residual saturation*. When the contaminant is at or below its maximum residual saturation, it will not move in the soil. The American Petroleum Institute[2] recommends the following equation to relate the amount of soil required to immobilize the contaminant:

$$C = (0.20^{*}V)/P^{*}\,\mathrm{Sr} \tag{2-1}$$

where

C = the cubic yards of soil required to immobilize the contaminant
V = volume of contaminant in barrels
P = porosity of the soil
Sr = residual saturation

While this equation was originally developed for petroleum-based compounds, the relationships expressed by the formula are valid for other compounds. The material that is adsorbed in the soil has a reduced chance of contaminating the groundwater. The portion of the material that is soluble in water will be picked up by rainwater on its movement through the ground and acts as a continuing source of contamination. The contaminants that are volatile may also move through the vadose zone and contaminate the aquifer. The rest will remain in the vadose zone.

Without treatment or removal, the adsorbed material can greatly increase the duration of a groundwater remediation program, or if the compound is volatile, it can create a direct hazard. Volatile organic compounds (VOCs) move upward and laterally in the soil, entering structures and/or producing explosion hazards or simply nuisance odors.[3] Therefore, the organic material in the vadose must be addressed as part of the remediation. In most, if not all, groundwater remediation programs, the source of contamination must be addressed. The adsorbed material in the vadose zone is a potential source of contamination.

The problem lies in the fact that the material adsorbed on the soil particles may be difficult to find and remove. First, there is generally very little lateral movement in the unsaturated zone, unless there are confining deposits that divert the movement of free product. A free product recovery well is generally constructed near the origin of the compound release, if that site is known. Secondly, in addition to the components of the spill changing as a result of volatilization and absorption in water, the compounds can also be transformed by (1) the natural biota in the soil, (2) oxidation, (3) reduction, (4) hydrolysis, and (5) dehydrohalogenation. Soil bacteria or these other processes can change the structure of an organic compound. Therefore, the organics found in the soil may be different from the original organics released.

Traditional investigation methods for locating soil contaminant source areas include collection of discrete soil samples or passive soil-gas sampling. The problem with these methods is that numerous data points are needed to present an accurate picture of the magnitude of the potential source area. However, there is a balance between the monies expended to perform an investigation and collecting statistically representative data of the area of interest. Consequently, the data collected need to be evaluated with the understanding that actual conditions may differ somewhat from what is reflected in the data, and this needs to be factored into the design.

Considering discrete soil sampling, for example, a common practice is to collect a 5-gram (g) soil sample for analysis and to use the data to represent a given volume of impacted soil. The low-level of accuracy of this method can be brought to light by considering an area measuring approximately 20 feet wide by 20 feet long by 5 feet deep (i.e., 2,000 cubic feet) and assuming the collection of ten discrete samples to represent contaminant levels in the area. With the approximate weight of the area of interest at approximately 200,000 pounds, the mass of the ten samples analyzed would represent 0.00005 percent of the total volume of soil. Similarly, passive gas sampling methods involve the measurement of contaminant levels in the soil vapor collected from soil samples whose mass is very limited compared to the investigation area.

The resulting analytical results are representative of a small portion of the potential source area.

Despite their limitations, the investigation methods mentioned above can be used effectively in conjunction with other site assessment strategies. For instance, a more commonly used approach in site investigation is to perform a dynamic soil vapor test. This approach involves the installation of multiple sample points within the focus area and the induction of a vacuum to extract soil vapors for analysis. Using a methodical approach involving extraction and analysis of soil vapors from multiple points and installation of additional points based on the data, one can more accurately define the potential limits of the contamination. Once the potential source areas are better identified, discrete soil sampling can then be performed to verify soil contaminant levels in a more focused manner.

In addition to the soil vapor extraction test describe above, another method that has been developed for finding petroleum hydrocarbons in the vadose zone is carbon dioxide measurement.[4] As previously mentioned, soil vapor extraction tests detect small amounts of soil vapor over a wide area at a contaminated site. The test will pick up the VOCs that exist in the vadose zone. These compounds can be a direct result of adsorbed material or an indication of groundwater contamination. Only VOCs are detectable with this method.

An extension to the soil vapor extraction test is a carbon dioxide measurement. For this measurement, the soil vapor is tested for carbon dioxide instead of organic vapors. It has been shown that the natural biological degradation of the organic compounds results in raised levels of carbon dioxide in the vadose zone. The technical details of why this occurs are covered in Chapter 3. This method is limited to biodegradable compounds, and the results can be masked by natural organic material.

When found, the material can be removed in several ways. For shallow spills, the ground can be excavated and (1) biodegraded in a solid-phase bioreactor such as a landfarm or soil pile (if the organic is degradable), (2) buried in a controlled landfill, or (3) thermally treated. For deeper contamination, in situ treatment or vapor extraction systems (VES) are the main methods of treatment, although flushing and recovery have been used on occasion. The biological methods are covered in the next chapter.

Many of the same problems are encountered when the pure compound movement is stopped by an impermeable layer of soil. When the pure compound reaches the impermeable layer, its downward progress stops unless the impermeable layer is sloped, and gravity can continue to carry it laterally and vertically away from the release area. In most cases, the material spreads out atop the impermeable layer like a pancake. This process continues until the contaminant contacts enough soil to adsorb the entire spill, or the impermeable layer ends, and the contaminant continues downward under the influence of gravity.

The same problems exist for a cleanup of material that hits an impermeable soil layer, as in the cleanup of an adsorbed material. It is hard to gather the material in one spot so that it can be recovered or treated. A containment barrier such as a slurry wall can be installed to prevent the continued spreading of the contaminant. To be effective, the slurry wall would have to completely surround the spill and an impermeable cover system would need to be placed above the footprint of the slurry wall to provide full containment. Also, a well or wells could be drilled down to the impermeable soil, and the pure compound recovered. The well(s) would not be able to recover a significant portion of the pure compound spilled due to interstitial forces within the soils. Free product removal followed by in situ treatment or VES are typically the best methods of cleanup.

Finally, the spill can reach an aquifer. Depending on the relative density of the pure compound, the spilled material will either float atop the aquifer (referred to LNAPL), or sink to the bottom of the aquifer (referred to as DNAPL). Additionally, the contaminant solubility and aquifer porosity characteristics will dictate the contaminant concentrations in the groundwater. Typically, the soil porosity is represented by two systems, one immobile and the other mobile, where mass transfer occurs through molecular diffusion. That is, there exist primary flow paths along which the bulk of fluid movement occurs, as well as secondary channels that act as reservoirs for contaminant mass. This dual-domain model provides a physically based mechanism that accounts for both the primary solute transport along small-scale preferential flow paths, as well as mass storage and relief activity of relatively immobile solutes in low conductivity materials.[5]

If the aquifer must be cleaned, the treatment method or methods used for an organic cleanup will depend on several factors. All of the following will have to be considered when choosing the unit operations to be used:

A. Description of the release and remediation objectives
    1. Concentration
    2. Quantity of contaminant
    3. Total time allotted for cleanup
    4. Final use of the water

B. Properties of the spilled material
    1. Solubility
    2. Density
    3. Stripability
    4. Absorbability
    5. Biodegradability

C. Site and aquifer characteristics
    1. Depth to water
    2. Permeability
    3. Lithology
    4. Extent of contamination
    5. Ongoing site activities

Other factors will be important on individual projects. This chapter addresses the physical and chemical methods of removing organics from an aquifer. Chapter 3 reviews biological methods, and Chapter 4 covers the aboveground equipment needed for in situ methods of biological treatment and oxidation of organic compounds.

PURE COMPOUND RECOVERY

Pure compound recovery is possible only when the contaminant is not entirely soluble in water. After the organic is in solution, the pure compound recovery techniques will not work. The following sections provide information on physical characteristics of thirty organic compounds and discuss pure compound recovery options available in the market.

Physical Parameters

The selection of the best technology for pure compound recovery should be made by evaluating several site-specific factors, including the geology of the site, the hydraulic conductivity, water-table fluctuations, and the nature of the compound. The following sections discuss important physical parameters such as solubility, specific gravity, and the partition coefficient for the most common petroleum and chlorinated hydrocarbons.

Solubility

Table 1-2 (see p. 17) lists the solubility for thirty organic compounds. If the compound is not soluble, then it will either float atop the aquifer or sink to the bottom. The compound's relative position to the water in the aquifer will depend on the relative density of the material.

Organic compounds that are lighter than water will float, and organic compounds that are heavier than water will sink.

Very soluble compounds such as acetone and phenol cannot use pure compound recovery techniques. This also includes the situations when a surfactant or similar compound creates an emulsion. Straight-chain hydrocarbons are generally not very soluble in water. Most petroleum products (oil, gasoline, etc.) fall into this category. Chlorinated hydrocarbons are also not very soluble in water, with chlorinated solvents being the most common of the low- solubility chlorinated hydrocarbons.

Although chlorinated organics are poorly soluble in water, they still have some solubility, and as a pure compound can represent a potential long-term source of impacts to groundwater systems. The more chlorine substitutions, the less soluble the compound is in groundwater (Table 2-1). However, many can still show up in the low parts per million (ppm) range in the aquifer. Because the threshold level of taste for these compounds is also very low, people do notice their presence in drinking water, which is why they cannot go undetected in domestic drinking water systems for long periods of time. Some chlorinated hydrocarbons have been shown to cause cancer in laboratory animals.

There have been public outcries in the past about many of these organics entering the potable water system and, as a result, these compounds are currently regulated in drinking water systems, some to very low parts per billion (ppb) levels. The main part of the compounds after entering an aquifer will continue down through the aquifer until stopped by an impermeable soil layer above the water table or by the water table itself, or will continue downward until it encounters an impermeable soil layer within the aquifer unless it is bound in the residual phase within the aquifer matrix prior to encountering this layer. As with an impermeable layer in the unsaturated zone, the chlorinated compound will then spread like a pancake atop this layer.

Specific Gravity

Table 1-1 (see p. 16) provides the specific gravity of thirty organic compounds. Water is used as the reference compound for the specific gravities. Therefore, any compound with a specific gravity less than 1.00 would be lighter than water, and any compound with a specific gravity greater than 1.00 would be heavier than water. In general, petroleum-based compounds are lighter than water, and pure compounds of these fall under the category of an LNAPL. Chlorinated compounds are heavier than water, and pure compounds of these fall under the category of a DNAPL. Pure compounds from releases from gasoline stations, oil terminals, and pipelines will usually be found atop the water table. However, gasoline contains several types of organic ring compounds (benzene being the basic structure) to enhance the octane rating. These ring compounds are relatively soluble in water (Table 1-2), and while the main part of the gasoline will float, the soluble components will enter the water. This is also true for the alcohol component of "gasohol" gasolines.

The pure compounds from the release of industrial solvents containing compounds such as tetrachloroethene and trichloroethene will usually be found at the base of an aquifer, and similar to LNAPLs will leave a "trail" of residuals from the release site. Because tetrachloroethene and trichloroethene are partially soluble in water, these compounds will enter the groundwater and migrate in its flow direction.

Partition Coefficient

Table 2-1 lists the octanol–water partition coefficient for thirty organic compounds. This coefficient is a measure of the hydrophobicity and hydrophilicity of a compound. The octanol–water partition coefficient, or K_{ow}, could be used in modeling the migration of organic compounds in groundwater.

Henry's Law Constant, Carbon Adsorption Capacity, and Biodegradability

Henry's law constant (stripability), carbon adsorption capacity, and the biodegradability of these same thirty compounds are discussed in their respective treatment sections.

Recovery Methods

After the pure compound has entered the aquifer, it must be removed or contained, or it will be a continuous source of aquifer contamination. The remediation system design engineer should stress the importance of removing or containing contaminants as a pure compound. This section describes the two most common methods for pure compound recovery, including recovery wells and intercepting trenches. In addition, a section with a description of other methods that are used to address site conditions that are not conducive to the use of recovery wells or trenches is included at the end.

By far, LNAPLs are more easily removed than DNAPLs. A floating material can be more easily removed from an aquifer for the following reasons: (1) it is shallower, floating atop the water table rather than being deeper at the base of an aquifer; (2) the water in the aquifer

TABLE 2-1 Octanol Water Coefficients (K_{ow}) for Specific Organic Compounds

	Compound	K_{ow}	Reference
1	Acetone	.6	1(D)
2	Benzene	131.8	1(A)
3	Bromodichloromethane	75.9	2
4	Bromoform	251.2	1(B)
5	Carbon tetrachloride	436.5	1(A)
6	Chlorobenzene	691.8	1(A)
7	Chloroform	93.3	1(A)
8	2-Chlorophenol	145.0	2
9	p-Dichlorobenzene (1,4)	3980.0	1(A)
10	1,1-Dichloroethane	61.7	1(A)
11	1,2-Dichloroethane	30.2	1(A)
12	1,1-Dichloroethylene	69.2	1(A)
13	cis-1,2-Dichloroethylene	5.0	1(A)
14	trans-1,2-Dichloroethylene	3.0	1(A)
15	Ethylbenzene	1412.5	1(A)
16	Hexachlorobenzene	169824.4	1(A)
17	Methylene chloride	19.9	1(B)
18	Methylethylketone	1.8	1(A)
19	Methyl naphthalene	13000.0	2
20	Methyl tert-butyl-ether	NA	
21	Naphthalene	2760.0	2
22	Pentachlorophenol	100000.0	1(B)
23	Phenol	28.8	1(A)
24	Tetrachloroethylene	398.1	1(A)
25	Toluene	134.9	1(A)
26	1,1,1-Trichloroethane	316.2	1(B)
27	1,1,2-Trichloroethane	295.1	1(A)
28	Trichloroethylene	239.9	1(A)
29	Vinyl chloride	24.0	1(A)
30	o-Xylene	891.3	1(C)

NA = Not available.

1. *Superfund Public Health Evaluation Manual*, Office of Emergency and Remedial Response Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, 1986.
   A. Environmental Criteria and Assessment Office (ECAO), EPA, *Health Effects Assessments for Specific Chemicals*, 1985.
   B. Mabey, W. R., Smith, J. H., Rodoll, R. T., Johnson, H. L., Mill, T., Chou, T. W., Gates, J., Patridge I. W., Jaber H., and Vanderberg, D., *Aquatic Fate Process Data for Organic Priority Pollutants*, EPA Contract Nos. 68-01-3867 and 68-03-2981 by SRI International, for Monitoring and Data Support Division, Office of Water Regulations and Standards, Washington, D.C., 1982.
   C. Dawson, et al., *Physical/Chemical Properties of Hazardous Waste Constituents*, by Southeast Environmental Research Laboratory for USEPA, 1980.
   D. *Handbook of Environmental Data for Organic Chemicals*, 2nd edition, Van Nostrand Reinhold Co., New York, 1983.
2. USEPA *Basics of Pump-and-Treat Ground-Water Remediation Technology*, EPA/600/8-90/003, Robert S. Kerr, Environmental Research Laboratory, March 1990.

can be used to direct the movement of the floating compound; and (3) residuals entrained in the soil matrix above the water table make them accessible to removal mechanisms such as soil vapor extraction, whereas residuals for DNAPLs are present both above and below the water table. Figure 2-1 shows LNAPL floating on the water surface at the top of an aquifer. The LNAPL will vary with fluctuations in the water table, although in certain geologic settings, raising water levels will trap some residuals in the aquifer matrix just below the water table.

DNAPLs are very difficult to remove from an aquifer because they get entrained not only in the vadose zone but also within the saturated zone as the DANPL migrates downward within the aquifer. Where LNAPLs will spread out atop the groundwater surface, DNAPLs will spread out atop the confining units.

Recovery Wells

Figure 2-2 shows a well being placed in the middle of the spill area. When groundwater is removed, a depression is formed in the water table in the immediate vicinity of the well, causing the LNAPL to

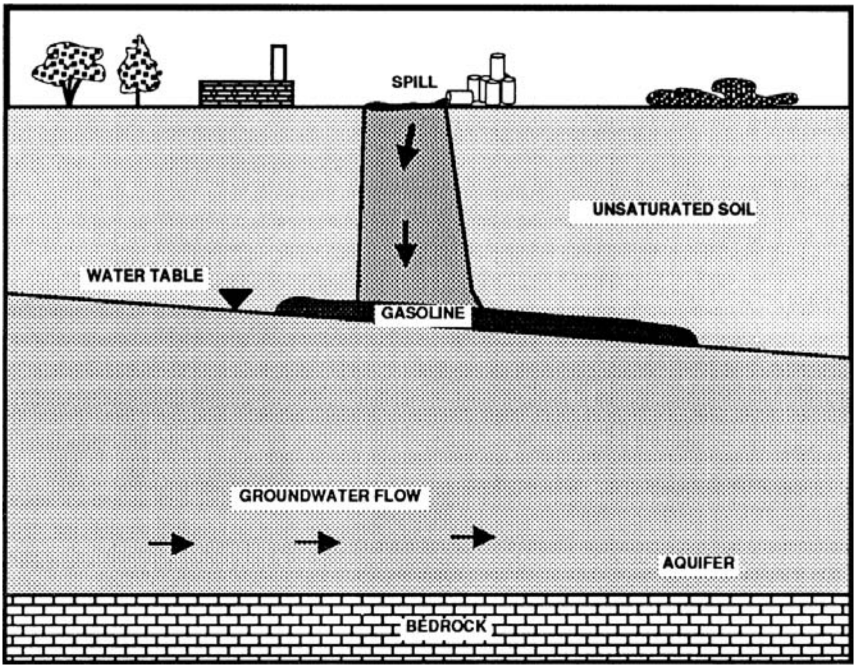

FIGURE 2-1. Petroleum product floating atop an aquifer.

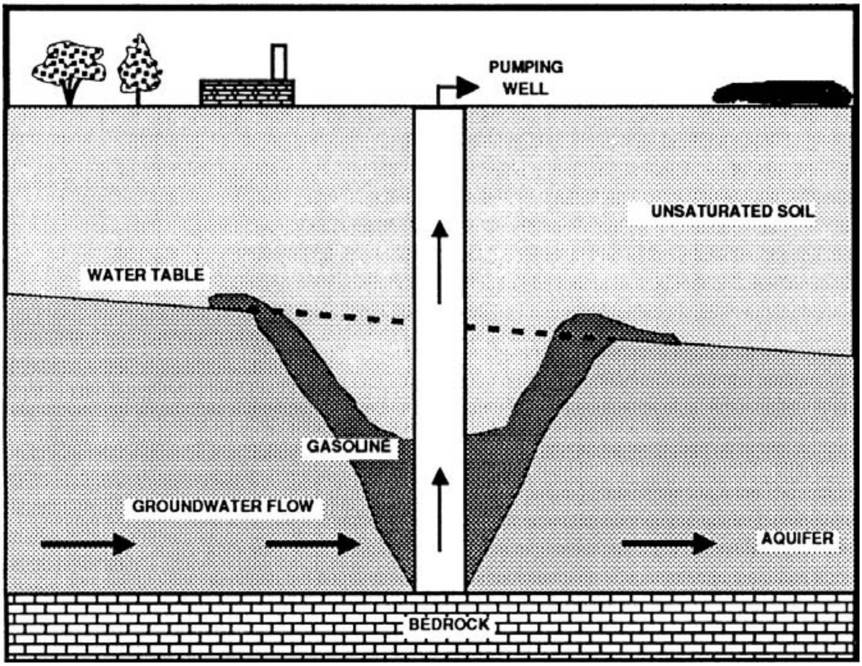

FIGURE 2-2. Collection of petroleum product by water drawdown.

flow toward the recovery well. Upon entering the well screen, various types of pumping systems are available to remove the LNAPL, and these pumping systems are discussed in later sections of this chapter. The design engineer needs to balance the number of recovery wells needed to remove the LNAPL with the cost of the recovery system. Although in many cases sufficient groundwater can be pumped from a single well so that groundwater levels are lowered enough to control the entire spread of the LNAPL, this is not often desirable. The reason for this is that as the LNAPL is moving toward the recovery well it is being entrained in the aquifer matrix (residuals) and never reaches the well. The alternative is to install more than one well to recover the LNAPL, generally minimizing the amount of residuals entrained and decreasing the time required to remove the LNAPL.

Where depressing the water table with pumping is a strategy that can be used to cause LNAPLs to move toward a recovery well, that strategy is not available for DNAPLs. If that strategy is applied to DNAPLs, large volumes of groundwater would need to be removed with little benefit on enhancing the recovery of DNAPL. The strategy that is often utilized, if recovery of DNAPLs is part of the overall remediation strategy for a site, is either to manually bail the well on a periodic basis (often monthly) using a bottom fill bailer to minimize groundwater collection or to install an automated recovery system that focuses on DNAPL recovery and minimizes groundwater recovery.

In-well Methods

When LNAPL is accumulating in the well, there are several methods to remove it. The first is to lower a bailer into the well and let the floating material pour over the top of the bailer. The lip of the bailer is kept above the water level so that only the contaminant is removed. This process is time-consuming and manpower intensive. Several manufacturers have automated this process.

The bailers have been weighted so that they float in water and sink in anything lighter than water. The same unit can contain a pump for the water to maintain a depression in the water table and a timer to raise and lower the bailer. After the well is drilled and the equipment is set up, periodic visits are required not only to check the equipment, but also for management of the recovered fluids. Specifically, what typically occurs is that both LNAPL and groundwater are recovered (often referred to as *total fluids*). The recovered liquid is then either containerized for subsequent disposal as a bulk liquid or it is first treated using an oil/water separator, with each stream managed individually (LNAPL versus impacted groundwater). The decision whether to include a separation technology depends on the volume of LNAPL being recovered and consequently on the cost of bulk disposal versus the cost of purchasing and maintaining an oil/water separator. Total fluids recovery is discussed further later in this chapter.

Figure 2-3 and 2-4 show an even more advanced method of LNAPL removal. This system, once again, uses a pump to maintain the water table. An oil/water separator is placed in the well. A screen in the separator is coated with a hydrophobic material. The screen will not allow water to pass, but a petroleum-based product like gasoline can enter the separator. The screen surrounds a second pump that removes the LNAPL from the well. This system can remove higher quantities of material.

Another method combines concepts from the first two methods and can be used with or without a water-table depression pump. A pneumatically driven skimmer device has been designed to sink in any fluids lighter than water and float just above the water table. The intake that floats just above the water table is made of a hydrophobic material to prevent water from entering the intake. A pneumatic bladder pump is set up to operate from essentially 0 to 5 gpm. The

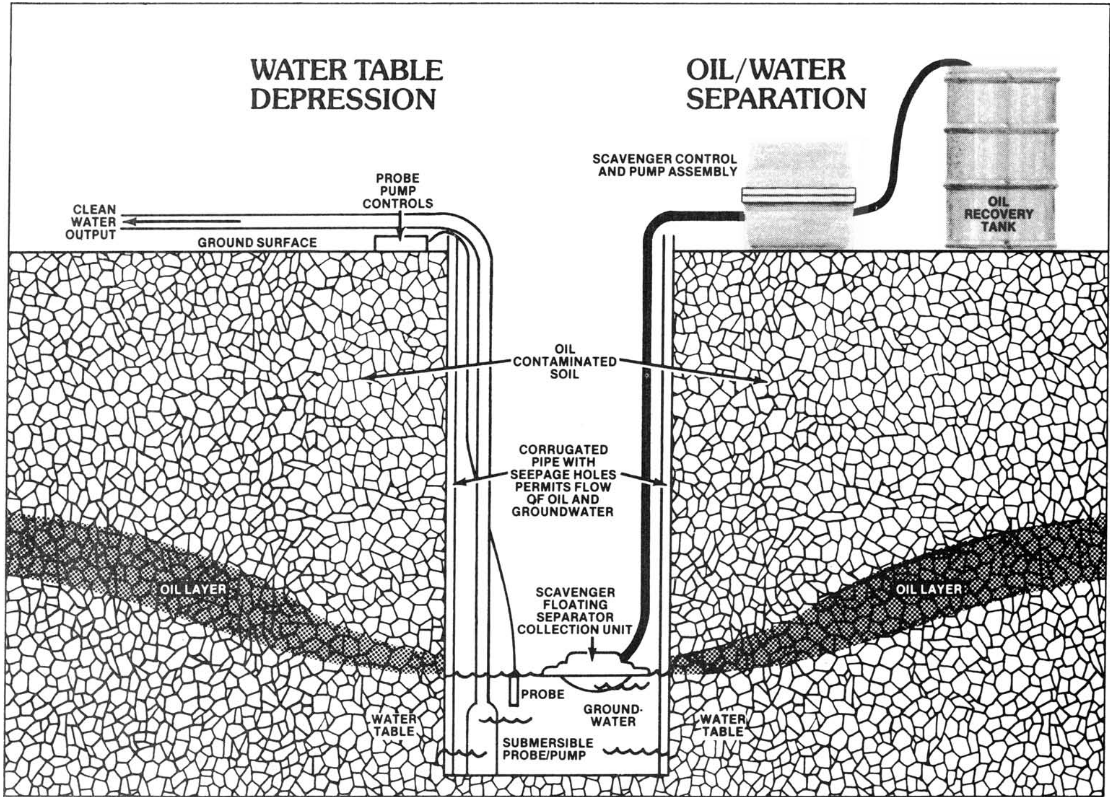

FIGURE 2-3. Oil/water separation in the well. (Courtesy of Oil Recovery Systems, Inc.)

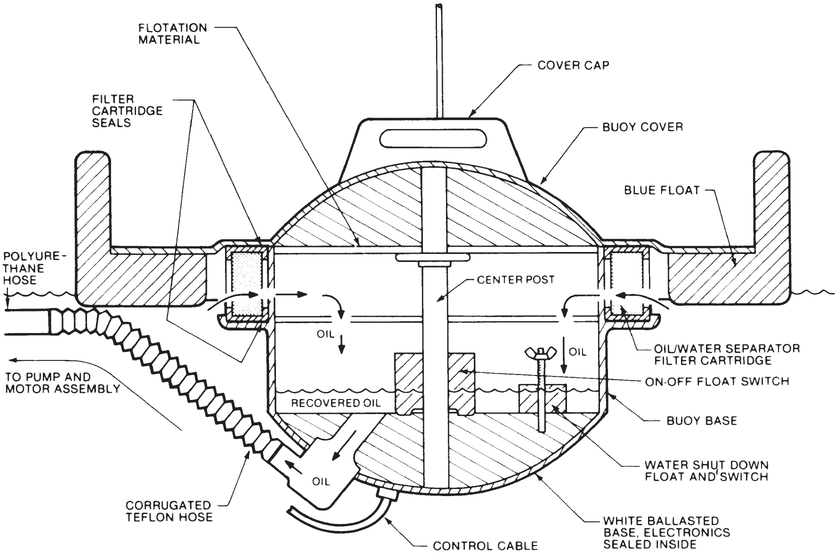

FIGURE 2-4. Oil/water separator. (Courtesy of Oil Recovery Systems, Inc.)

float is suspended from a coil of tubing, allowing the float to rise and fall with fluctuations in the water table.

When the material is too viscous to move through the screen or when there is a large amount of LNAPL, a third method can be used. This method requires a large-diameter well. Once again, two pumps are used. In this case, the LNAPL recovery pump is controlled by a conductivity probe. Water carries an electrical charge between two electrodes. LNAPLs do not conduct electricity. When the probe is immersed in an LNAPL, no charge passes between the two electrodes of the probe. The unit then knows that it is in a pure compound and turns on the second pump. Figure 2-5 shows a conductivity removal method. One problem with this method is that fluctuating water-table conditions can require that LNAPL recovery pumps be raised or lowered throughout their operation.

One final common method is used with the recovery of LNAPLs. For wells with a small diameter (≤4 inches) that yield low flows (i.e., less than 5 gpm), a pneumatic submersible pump can be used. These pumps can be set three ways: (1) to recover LNAPLs (intakes located at the top of the pump); (2) to recover total fluids (intake located at both the top and the bottom of the pump), which is a combination of both LNAPLs and groundwater; or (3) to recover DNAPLs (intake located at bottom of pump).

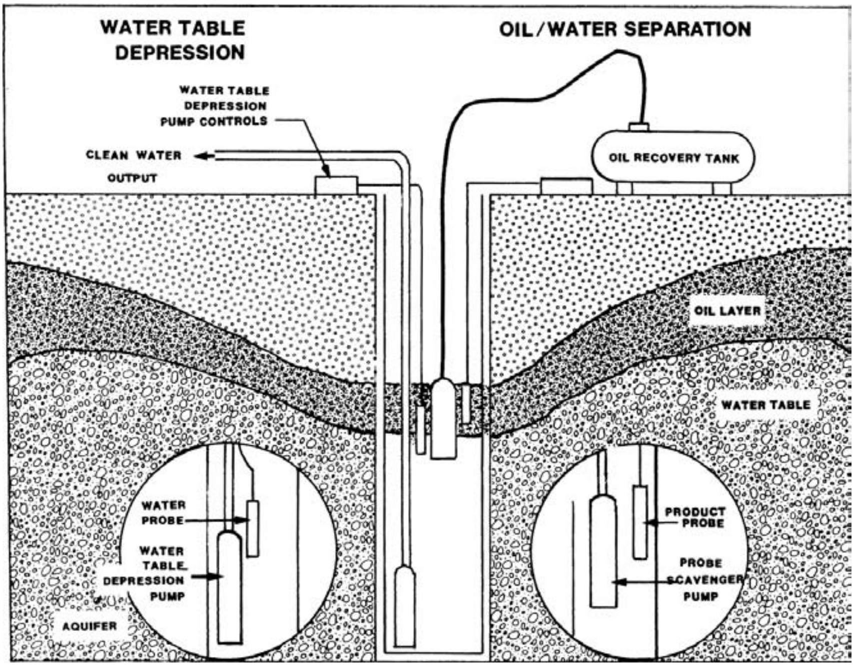

FIGURE 2-5. Oil recovery with a product pump controlled by a product probe.

All five methods described above have been used on many installations. Several manufacturers have a broad base of experience with each of these methods. One of these companies should be contacted to assist on pure compound recovery.

Total Fluids and Separation

Where hydraulic control is required and/or a cone of depression is required to mobilize LNAPLs toward the well and where hydraulic conductivity/permeability is relatively low, it is frequently more practical and cost effective to extract both groundwater and LNAPL together and separate the fluids aboveground using an oil/water separator. A principal advantage of total fluids extraction is that relatively small-diameter wells can be used instead of the bigger wells required for a dual-pump arrangement of a submersible pump and skimmer pump within the same borehole.

A similar system can also be used for DNAPLs and offers the same advantages as with LNAPLs in that small diameter wells can be used. With DNAPLs, the recovered fluids would be discharged to a tank where the DNAPLs could accumulate at the bottom, and groundwater discharges over the top. A system would be set up to minimize the accumulation of DNAPLs at the bottom of the tank by removing these for temporary storage and disposal.

Intercepting Trench

One other way to remove nonflammable LNAPLs is to dig a trench in the path of the groundwater movement (Figure 2-6). This technique works best for high water tables and other conditions (i.e., perched water tables) where the spill stays near the surface. As the groundwater enters the trench, the LNAPL remains atop the water. However, when the LNAPL is in the trench, the floating material can be removed by skimmers or other standard surface removal devices. The water level in the ditch can be lowered to increase the rate of LNAPL movement. Once again, the water in the aquifer is used to control the movement of the LNAPL. Special designs of this method must be considered if the LNAPL is flammable or if it represents an explosion hazard.

Trenches are usually not used for DNAPLs because of the depths involved. They could be successfully used only in geologic settings where the DNAPL has pancaked atop a confining layer located at a shallow depth.

DNAPLs may or may not move in the direction of the groundwater. Therefore, a change in the groundwater flow may or may not affect

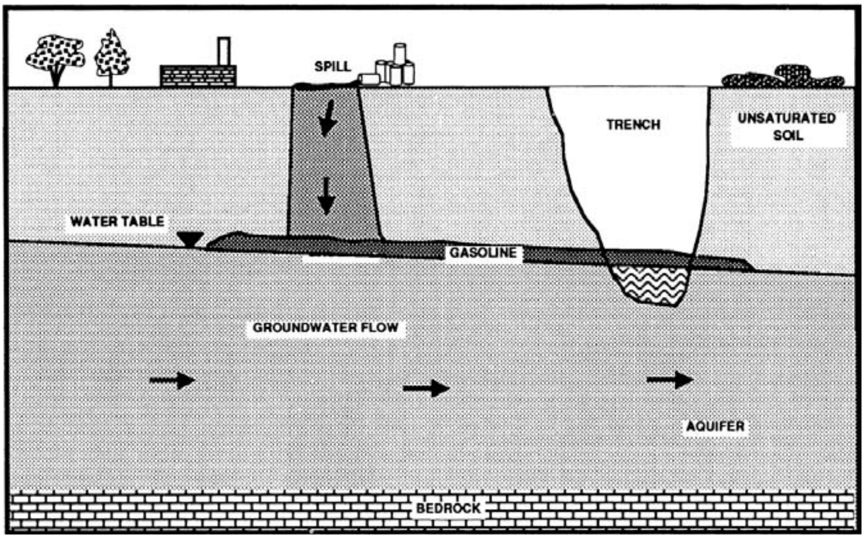

FIGURE 2-6. Removal of floating material by an intercepting trench.

the movement of the compound. In particular cases when wells can be used to force the DNAPLs in a particular direction, the process will not be as efficient as with a floating material. In some cases, the compound can travel in the opposite direction of the groundwater flow. Figure 2-7 shows a case where the impervious layer at the bottom of the aquifer slopes in the opposite direction of the groundwater flow. The DNAPL will continue to be affected by gravity and travel with the contour of the aquifer bottom and not necessarily the direction of the groundwater flow.

In summary, when a pure compound is released to the ground, we must consider several important factors to clean up the release. We must first determine if the material has reached the aquifer. We then must discover if the material has stayed atop the aquifer, dissolved into the water of the aquifer, or passed down through the aquifer. If the material is not in the aquifer, then one of the pure compound treatment methods should be used to recover as much of the material as possible.

As previously discussed, recovery of either LNAPL or DNAPL often results in the additional recovery of dissolved-phase VOC-impacted groundwater. This water will require treatment prior to

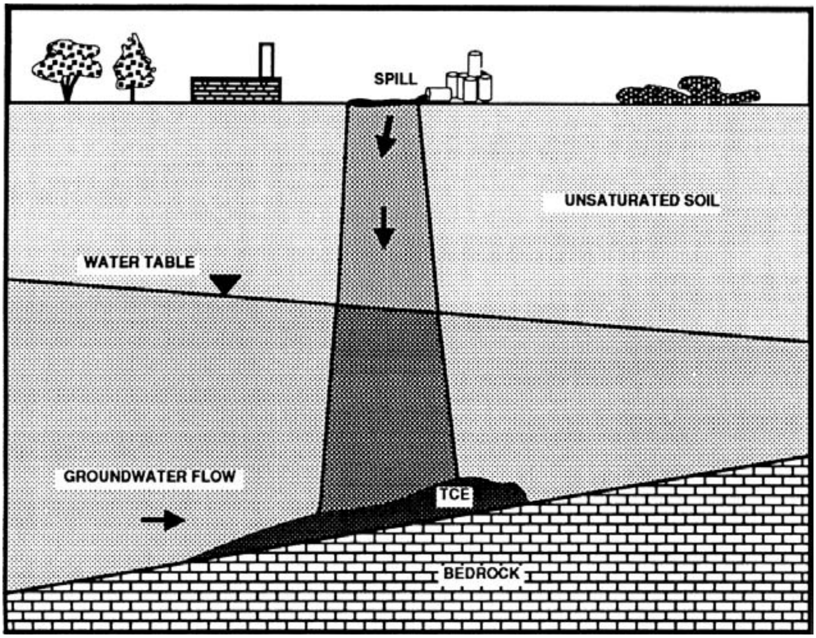

FIGURE 2-7. Chlorinated hydrocarbon movement in opposite direction of groundwater flow.

disposal. The following section discusses one of the commonly used ex situ treatment technologies in the industry, air stripping. The remainder of this chapter and Chapter 4 cover additional treatment technologies for managing the dissolved phase when it enters the aquifer and migrates in the direction of groundwater flow.

AIR STRIPPING

Aeration has been used for decades for the removal of dissolved gases, such as carbon dioxide, hydrogen sulfide, and ammonia, from water and wastewater. It has also been used to introduce oxygen as a means of increasing dissolved oxygen content and for oxidation of dissolved metals such as iron. It wasn't until the mid-1970s that the technology was applied for the treatment of water with low levels of synthetic (VOCs).[6]

Aeration relies on the exposure of the contaminated water to a fresh air supply. As the air and water mix, the volatile compounds in the water are driven out of solution and into the vapor state. Maximizing air/water contact is the key to any aeration system.

Aeration Technologies

The two major types of components used for air stripping are towers and aerators, while the principal factor for the selection of the type of component is the desired degree of removal and the Henry's law constant of the compound. Aeration basins consist of diffused aeration or mechanical aeration; stripping towers include packed towers, trayed towers, and spray systems. Numerous technologies are listed in Table 2-2. Among these, packed-tower aeration was the most commonly used for the removal of VOCs from water[7] for many years, with low-profile tray strippers growing in popularity within the past ten years. Selection of the most appropriate technology has to take into account the target contaminants, air/water flow rates, the target removal efficiency, physical constraints (access limitations), subsequent treatment of the airstream (if needed), and operation and maintenance considerations. The following sections discuss various aeration technologies commonly used.

Aeration Basins

Aeration basins are straightforward and relatively low-cost technologies and may be used for situations in which VOCs are present, and

TABLE 2-2 Common Aeration Technologies

Device References	Typical Configuration	Removal*	Cost($/1000 gal)
Slat tray aerator	Redwood slat trays in box-like structure 10 to 18 feet tall. Countercurrent air/water flow.	60% to 80%	$0.05
Diffused air	Water storage basin with air diffusers. Up to 20 minute contact times common.	<90%	$0.40 to $2.00
Spray aeration	Spray nozzles in open or closed system. Fine droplets provide air/water contact.	50% to 90%	NA
Cascade aerator	Exposed system of stacked trays, relies on natural draft.	50%	$0.05
Packed column	Cylindrical with plastic media. Countercurrent air/water flows.	90% to 99.9%	$0.05 to $0.25
Rotary stripper	Rotating packed bed. Relies on centrifugal force to form thin liquid films and high turbulence.	>90%	NA

*Removal of Trichloroethylene.
NA = Not available.

low efficiencies are allowed. An aeration basin is a continuous-flow tank with air diffusers placed at the bottom to provide an increased gas-phase surface area for the mass transfer of the VOCs. The bubbles form the surface area for transfer between the groundwater and the air. The mass transfer driving force is low because of dilution, but the performance can be improved by placing baffles in the tank that will increase the driving force for the mass transfer.

Diffused air or bubble aeration air strippers are mainly applied to small flows, less than 50 gpm, and in situations that have high iron content or other material that may foul the packing of a packed-tower air stripper. Basically, design engineers have been finding that the maintenance cost of a packed-tower air stripper is the controlling design parameter in small systems. If elevated concentrations of iron are present in the water, then a low-maintenance system like a diffused aeration system is preferable.

These systems can also be designed to be compact and portable and can be shaped to completely fit into small buildings at a treatment site. Certain designs, such as D2M2 in Figure 2-8, also add filtration directly in the unit to produce high-quality effluent from the air stripper. This technology has been widely used for gas station cleanups because of its ease of operation and flexibility for application over a wide range of low-flow conditions. Innovative manufacturers have devised methods of cascading the water being treated through a series of aeration

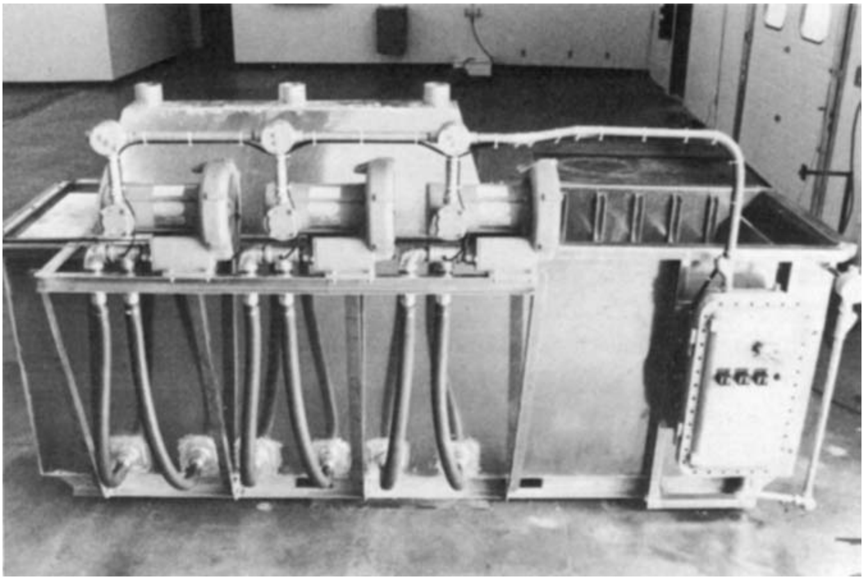

FIGURE 2-8. D2M2 air stripper. (Courtesy of Geraghty & Miller, Inc.)

chambers to increase efficiency of the bubble aeration process. These systems offer a low profile while taking up a relatively small amount of space.

Packed, trayed, and spray towers increase the surface area of the groundwater available for mass transfer. The water cascades down a tower of slats or structured packing material while air is drawn through the tower by a fan. Treatment efficiencies are moderate to high because of plug flow of the water and because cascading droplets of water provide an additional surface area of mass transfer.

There are a number of types of tray aerators, all based on the same design concept of stacked trays. In these designs, water is distributed over the top tray with a spray nozzle and then flows from the upper tray over the tray sides into lower trays. Air is forced in below an orifice tray that contains a flowing water stream. The airflow is designed to maintain "froth" in the tray to provide the mass transfer required. Trays can be stacked and run in series to increase system performance, or water flow rate can be reduced over a single tray to enhance removal efficiency. Because there is no packing, the potential for fouling is reduced. These systems require a great deal of energy and are not cost effective above flows of approximately 100 gpm.

Stripping tower technology has been used in several groundwater cleanup cases using a spray basin. In these systems, a piping grid is laid out over the area of a basin (either earthwork or concrete), and spray nozzles are placed evenly throughout the area to spray the contaminated area water into the air in very fine droplets. The water is collected in the basin and pumped off or, in the case of an earthwork recharge basin, allowed to percolate back into the ground. This method is often used to flush out an area of contaminated soil. The advantage of this system is its extremely low capital cost, which makes it ideal for a cleanup of a temporary nature. The disadvantages are that large tracts of land may be required and neighboring properties may be affected by wind-driven mists or, in winter, ice crystals. Extra pumping costs may also be incurred to provide adequate pressure to the nozzles. Finally, regulatory concerns will have to be satisfied when spraying hazardous waste onto land.

Packed Towers versus Tray Aerators

The advantages of using a tray tower over a conventional packed tower are that the tray tower is smaller and more compact and the elimination of packing results in lower maintenance costs. This is important when the space available for placement and maintenance of the equipment is limited (e.g., inside of a facility). The primary disadvantage is that to achieve a given removal efficiency the tray aerator requires a significantly higher airflow than a conventional packed tower. Additionally, tray aerators are typically limited to lower water flow rates than packed towers, thus several units may be required to treat the design flow rate for the system. Consequently, the operational costs can be greater for the tray tower. Thus, while either type of system can be used to achieve treatment goals, selection of the most appropriate aeration system is largely dependent on site-specific and economic constraints.

DESIGN OF PACKED TOWERS

While the government and industry have historically settled on packed-tower aeration as the main type of air stripper to be used, it is important to remember that packed-tower aerations are only one type of air stripper. Specific situations may require other aeration designs as the best technical and economic choice of treatment system. Small flows (<25 gpm) and high iron content are two examples of factors that may lead to alternative designs. However, because packed-tower aeration is the method of air stripping that has found the most acceptance for both potable water purification and remedial work on groundwater contamination, the majority of the discussion that follows is centered on packed-tower aerations. Much of what follows is also equally valid for other methods of air stripping.

Air stripping is a mass transfer process. In packed-tower aeration systems, air and water are run countercurrent through a randomly dumped or structured media. The media enhances air/liquid contact by breaking the water into thin films and exposing a large amount of liquid surface area to the air. The more surface area exposed, the greater the opportunity for transfer of the VOCs from the water into the passing air. The media also serve to continually mix the water so that the stripping process is not limited by diffusion of the VOCs through the water. The air carries the contaminants from the stripper and into the atmosphere or to an air treatment system. When the VOCs are discharged directly to air, they are dissipated by the velocity of the airstream and by any wind currents, where the chemicals may breakdown by natural ultraviolet (UV) degradation or other methods (chemical, biochemical, etc.). The treated water passes from the column for use, discharge, or further treatment, if required, as depicted in Figure 2-9. In some situations, local regulations and/or the level of VOCs emitted in the contaminated airstream necessitate the use of treatment technologies for the airstream. Several common air treatment technologies are discussed later in this chapter.

When sizing a packed column, the design engineer has three basic variables to define: (1) tower cross section, (2) tower height, and (3) air-to-water ratio. While these variables are dependent on each other (i.e., a change in air-to-water ratio may allow, or require, a change in packing height), the following basic relationships are helpful in preliminary sizing estimates:

Tower cross-sectional area is most strongly a function of water flow rate. The cross-sectional area of a tower will be determined by the flow rate and the liquid loading rate, the latter commonly ranging between 15 and 35 gallons per minute per square foot (gpm/ft^2).

Tower height is most strongly a function of the stream concentration and the removal efficiency required; the greater the efficiency required, the taller the tower. The treatment efficiency for a given incremental bed depth is constant; i.e., if 10 feet of packing achieves 90 percent removal, an additional 10 feet will achieve 90 percent of what remains, for a total of 99 percent removal.

Air-to-water ratio is a function of the contaminant being removed. The more volatile a substance is, the smaller the volume of air required to strip that compound. Air-to-water ratios range from 10:1 to 200:1, depending on the compound being removed.

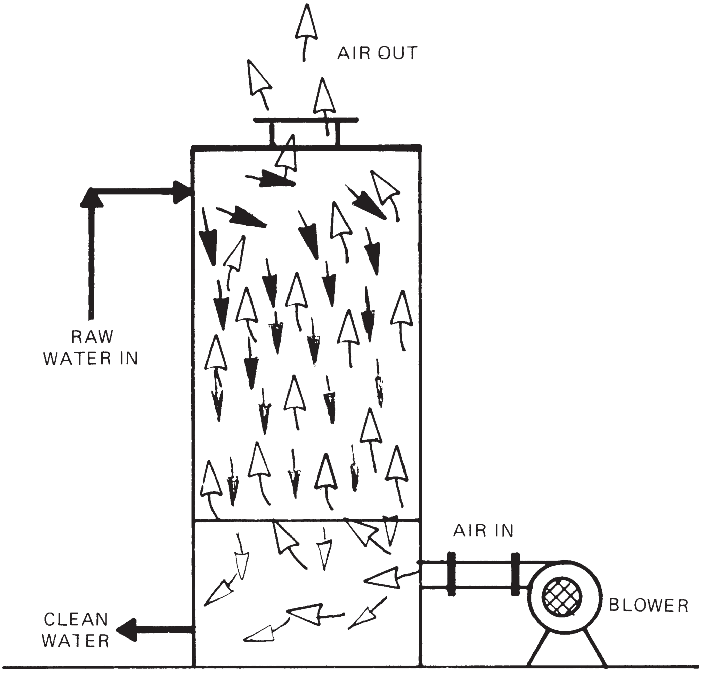

FIGURE 2-9. Packed-tower air stripper.

Another important variable in air-stripping design is the water temperature. Water temperature influences the air-stripping process in that higher temperatures enhance constituent volatility. In general, the design engineer must be aware of the temperature of the water that is to be treated. Groundwater temperatures vary throughout the country, and pretreatment equipment may raise or lower the temperature of the water entering the air stripper. Ambient temperature strippers experience little, if any, change in operating performance between winter and summer operation, although air temperatures may fluctuate over a 100 degrees Fahrenheit (°F) range. This is because the groundwater temperature stays at or near a constant temperature year round, and the thermal mass of the water is much greater than the thermal mass of the air in a stripper. Thus, the actual operating temperature of the stripper remains fairly constant.

The temperature may be changed through the use of preheaters on the water stream or injection of steam directly into the tower. Stripping will occur at a higher rate at elevated temperatures, and some compounds that are barely volatile at ambient temperatures can be totally removed by raising the column temperature into the 140 to

180°F range.[9] The use of high-temperature strippers, or steam stripping, is generally limited to hazardous waste site cleanups of short duration or in situations with high levels of organics where air treatment is required. The limitation of high-temperature or steam strippers is chiefly the result of the high operating costs associated with heating the process streams.

The design method of any packed column starts with the basic mass transfer process. The rate of transfer of the VOCs will be a function of the driving force (the concentration gradient between water and air) and the air/water interface area. Different compounds will be transferred at different rates, depending on the contaminants Henry's law constant. The Henry's law constant is the ratio of the partial pressure of a compound in air to the mole fraction of the compound in water at equilibrium. Compounds with a high Henry's law constant have a greater concentration in air when an air/water system is in equilibrium. These compounds undergo a phase change from the dissolved state to vapor quite easily, and hence are easily stripped. Compounds with low Henry's law constants, on the other hand, are more hydrophilic and are more difficult to strip. Table 2-3 provides the Henry's law constants for thirty organic compounds at a fixed temperature. The Henry's law constant varies with temperature. Table 2-4 lists the functional relationship of the Henry's law constant and temperature for several common VOCs.

The mass transfer equations for an air/water stripping system are as follows:

$$Z = \mathrm{HTU}^{*}\ \mathrm{NTU} \tag{2-2}$$

$$\mathrm{HTU} = L^{1}/K_{\mathrm{la}} \tag{2-3}$$

$$\mathrm{NTU} = [R/(R-1)]^{*}\ \ln\left\{[(C_{\mathrm{inf}}/C_{\mathrm{eff}})^{*}(R-1)+1]/R\right\} \tag{2-4}$$

where

$R = (H^{*}G)/(L' * P)$
HTU = height of transfer unit (feet)
NTU = number of transfer units (unitless)
H = Henry's law constant (standard atmosphere [atm])
G = gas loading rate (cubic foot per minute [cfm])
L^{1} = liquid loading rate (gpm/ft^2)
P = operating pressure (atm)
Z = packing height (feet)

TABLE 2-3 Henry's Law Constants for Specific Organic Compounds

	Compound	Henry's Law Constant[a] atm	Reference
1	Acetone	0	1
2	Benzene	230	1
3	Bromodichloromethane	127	1
4	Bromoform	35	3
5	Carbon tetrachloride	1282	1
6	Chlorobenzene	145	2
7	Chloroform	171	1
8	2-Chlorophenol	0.93	2
9	p-Dichlorobenzene (1,4)	104	4
10	1,1-Dichloroethane	240	1
11	1,2-Dichloroethane	51	1
12	1,1-Dichloroethylene	1841	1
13	cis-1,2-Dichloroethylene	160	1
14	trans-1,2-Dichloroethylene	429	1
15	Ethylbenzene	359	1
16	Hexachlorobenzene	37.8	2
17	Methylene chloride	89	1
18	Methylethylketone	1.16	2
19	Methyl naphthalene	3.2	2
20	Methyl tert-butyl-ether	196	1
21	Naphthalene	20	4
22	Pentachlorophenol	0.15	2
23	Phenol	0.017	2
24	Tetrachloroethylene	1035	1
25	Toluene	217	1
26	1,1,1-Trichloroethane	390	1
27	1,1,2-Trichloroethane	41	2
28	Trichloroethylene	544	1
29	Vinyl chloride	355000	3
30	o-Xylene	266	1

[a] = at water temperature 68°F.

1. Per Hydro Group, Inc., 1990.
2. Solubility and vapor phase pressure data from *Handbook of Environmental Data on Organic Chemicals*, 2nd edition, by Karel Verschueren, Van Nostrand Reinhold, New York, 1983.
3. Michael C. Kavanaugh and R. Rhodes Trussel, "Design of aeration towers to strip volatile contaminants from drinking water", *Journal AWWA*, December 1980, p. 685.
4. Coskun Yurteri, David F. Ryan, John J. Callow, Mirat D. Gurol, "The effect of chemical composition of water on Henry's law constant", *Journal WPCF*, Volume 59, Number 11, p. 954, November 1987.

C_{inf} = influent concentration (micrograms per liter [μg/L])
C_{eff} = effluent concentration (μg/L)
K_{la} = overall mass transfer coefficient (sec^{-1})
R = stripping factor (unitless)

(*Note*: Unit conversion factors are not shown in the above equations. Units should be consistent.)

TABLE 2-4 Selected Henry's Law Constants As a Function of Temperature

$H(\text{atm}) = 10^{(b - a/T)}$ (T in Kelvin)

Compound	a	b
Trichloroethylene	1716	8.59
Tetrachloroethylene	2159	10.38
Benzene	1852	8.68
Toluene	1492	7.427

The key variables to define in the equations above are Henry's law constant (H) and the overall mass transfer coefficient (K_{la}). The Henry's law constant is available from a variety of sources; however, care must be taken in using the Henry's law constants because published values of Henry's law constants can vary by more than an order of magnitude. Additional theoretical research needs to be done in this area.

The mass transfer coefficient is a function of tower design and type of packing and is a good expression of the overall efficiency of the tower. Accurate quantification of this coefficient is very important; as can be seen from Equations 2-2 and 2-3, there is an inverse relationship between tower height and K_{la}. Thus, a 25-percent error in a K_{la} value might add 25 percent to the height of the tower, resulting in increased costs as a result of additional shell material and packing.

Because of this relationship, it is good engineering practice to select a mass transfer coefficient based on some type of field data, such as pilot test results or operating data from a similar installation on a similar water supply. Figure 2-10 shows a typical pilot system configuration. A pilot study on the actual water to be treated is best because chemical characteristics (such as the type and amount of contamination) will vary from source to source and may affect the stripping process. Pilot testing can be simple and inexpensive; usually enough data for design purposes can be obtained in a single day of testing. The testing should cover a range of possible liquid loading rates and air-to-water ratios, as the K_{la} will vary with both of these factors. The engineer selects a Henry's law constant value for the compound to be tested. He then varies the gas and liquid loading rate and measures the resulting effluent concentration for a constant influent concentration. The mass transfer equations can then be solved for the K_{la}.

When field data are not available or pilot testing is impractical or expensive, the use of theoretical correlations is acceptable. Correlations such as those developed by Onda, Sherwood and Holloway and Shulman[10] are commonly applied. These correlations were developed using bench-scale data to produce best fit curves to describe the

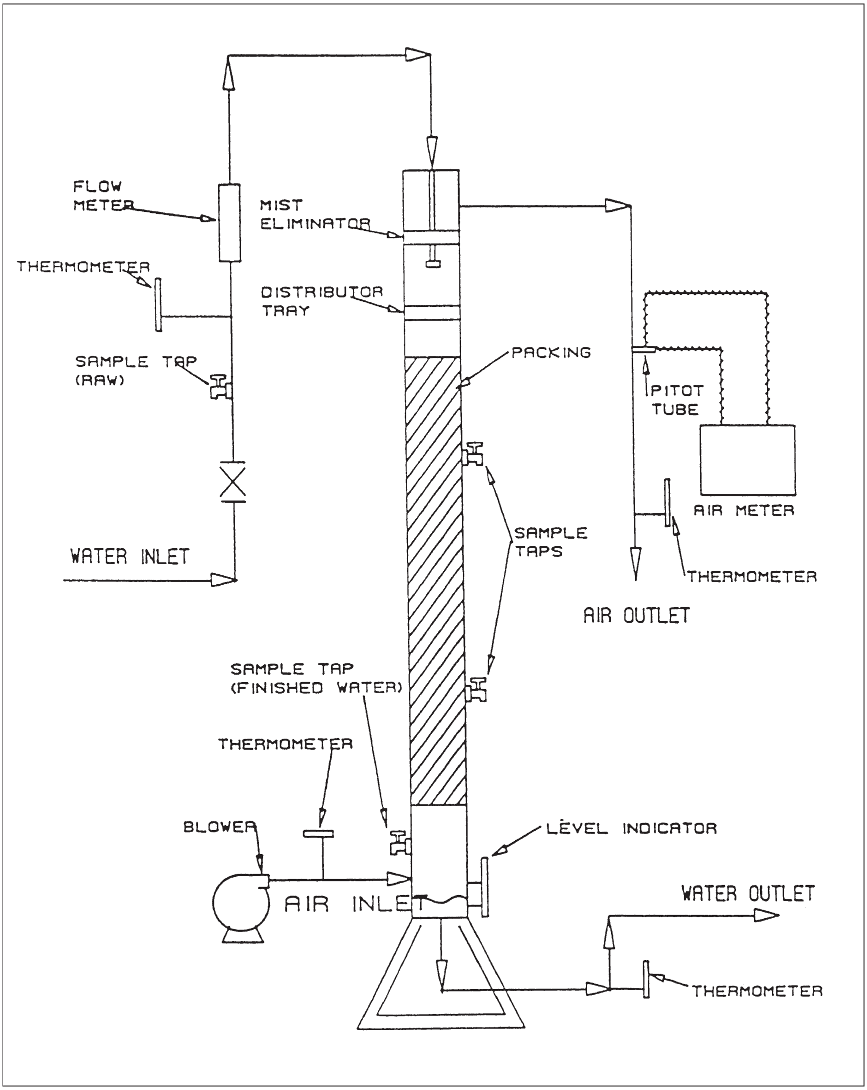

FIGURE 2-10. Pilot plant packed-tower air stripper.

relationship between the K_{la} and physical properties of the air, water, VOCs, and packing.

Published reports from a variety of sources[10–14] suggest that the Onda correlation is an acceptable means of evaluating air-stripper designs for an air/water countercurrent system. In one study, the Onda correlation provided the most accurate correlation of the three theoretical correlations mentioned above.[10] In a comparative study using published pilot scale data, the Onda correlation was found to provide a mass transfer rate (K_{la}) with an accuracy of ±30 percent.[14] In a later study,[6] the Onda correlation overestimated the K_{la} in 75 percent of the situations by an average of 37 percent. (For those cases, the Onda correlation would underestimate the packed bed depth, and the packed tower would fail to perform as designed.) The variations between Onda and the empirical data support the argument that adequate safety factors should be applied to any designs generated using the correlation.

When the Henry's law constant is known and a K_{la} determined for the range of water loading rates and air-to-water ratios of interest, then Equations 2-2,2-3, and 2-4 may be solved for different combinations of packing height and liquid loading rates. The design engineer can use these data to generate various tower configurations that will provide the required removal efficiencies. Some of these options can be eliminated based on site-specific constraints, such as a maximum allowable height. After these are removed, an estimate of capital costs and operating costs should be made for each tower, and a final tower design selected.

Cost Considerations

Cost of treatment can vary widely for packed towers, depending on the removal efficiency required, the compounds and concentrations involved, the supporting equipment required, and the need for air treatment. The capital cost of each of the processes discussed is closely related to the mass transfer efficiency of the process. In general, the lower the transfer efficiency, the larger the facility required for achieving a certain removal.

Operating cost is primarily a function of the hydraulics of the process and the method of gas dispersion. Equipment complexity or heavy maintenance is typically not a major consideration because most equipment is relatively simple, although it should be noted that fouling by chemical precipitation and/or biological growth must be controlled.

COLUMN COMPONENTS

The major components of a stripping tower are the tower shell, tower internals, packing, and air delivery systems as shown in Figure 2-11. The tower shell is usually cylindrical for strength and ease of fabrication and to prevent channeling of the air or water. Square or rectangular towers, while not common, are used particularly in situations where

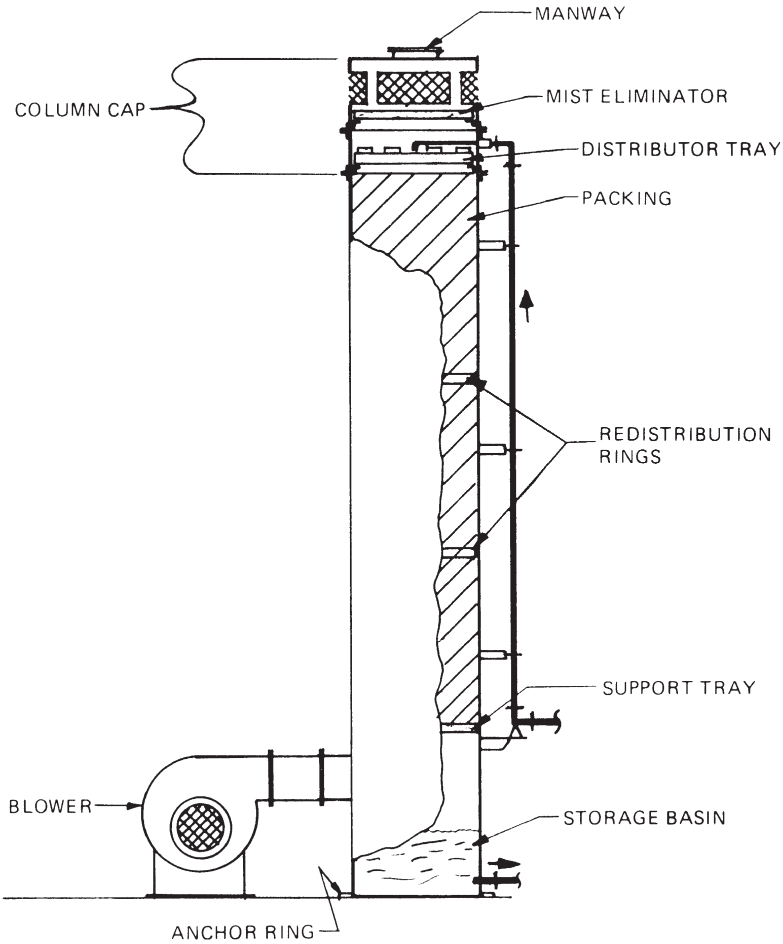

FIGURE 2-11. Packed-tower components.

the tower must be housed or when the tower shell is concrete. The tower must be built to withstand all applicable wind, snow, and earthquake loads for the area in which it is being installed and must be able to support the combined weight of the tower internals, packing, and the water held up in the tower. However, the tower does not need to be designed to support a full column of water because it will never be entirely filled with water during operation. Air openings at the bottom of the tower will allow water to drain out in case of an obstruction in the effluent water line, thereby acting as a safety outlet to prevent column flooding.

Construction Materials

Materials of shell construction include aluminum, fiberglass, stainless steel, coated carbon steel, and concrete. Fiberglass and aluminum are the least expensive, with stainless steel and coated carbon steel being slightly higher in cost in most cases. Concrete towers, typically with a brick face, are the most expensive. It is important to remember that raw material prices can fluctuate rapidly, so all applicable materials should be considered at the time of tower design. Costs aside, the relative advantages of the various materials hinge on their strength and corrosion resistance. Aluminum has excellent structural properties, is lightweight, and is suitable for potable water applications. It should not be used on highly acidic ($pH < 4.5$) process streams or where large amounts of chlorides or heavy metals are present. Fiberglass towers offer good corrosion resistance in most chemical environments (the hand layup method is preferred to filament-wound columns for chemical resistance) but is comparatively brittle, making it difficult to construct tall towers subject to wind loads.

The various stainless-steel alloys offer a wide range of corrosion resistance, as well as good structural properties, but many alloys are not readily available without paying premium prices. Carbon steel with an epoxy coating offers corrosion resistance and strength at low cost but requires increased maintenance costs for painting and periodic internal inspection.

Towers constructed of concrete are field erected. They provide high-quality aesthetics at a premium price. These units are also subject to honeycombing and leaks if the concrete is not properly poured. Table 2-5 summarizes the properties of the various materials of construction.

Air Exhaust Ports

The tower internals serve to ensure that the mass transfer process takes place under optimal conditions, at the most economical cost. Starting at the top of the tower, the first component that requires a design engineer's attention is the air exhaust ports. (For the purposes of this discussion, a forced draft tower will be discussed. Induced draft towers are explored later.) These ports are typically located around the circumference of the tower and sized to permit the air to escape with a minimum pressure drop. If the tower is for potable water, the outlets should be screened to prevent contamination by wind-borne material entering the tower; towers screened with 24-mesh screen have reported

TABLE 2-5 Packed Column Air Stripper—Materials of Construction

Material	Advantages	Disadvantages
Aluminum	—Lightweight —Low cost —Corrosion resistant —Excellent structural properties —Long life (>15 years) —No special coating required	—Poor resistance to water with pH less than 4.5 and greater than 8.6 —Pitting corrosion will occur in the presence of heavy metals. —Not well suited to high chloride water.
Carbon Steel	—Mid-range capital cost —Good structural properties —Long life if properly painted and maintained	—Requires coating inside and outside to prevent corrosion, leading to increased maintenance. —Heavier than aluminum or FRP.
Fiberglass	—Low cost —High chemical resistance to acidic and basic conditions, chlorides and metals	—Poorly defined structural properties. —Short life (<10 years) unless more expensive resins used. —Poor resistance to UV light (can be overcome with special coatings that must be maintained. —Requires guy wires in most situations. —Susceptible to extremes of temperature differential disturbing tower shape and interfering with distribution.
Stainless Steel	—Highly corrosive resistant Excellent structural properties Long life (>20 years) No special coating required	—Most expensive material for prefabricated towers. —Susceptible to stress fracture corrosion in the presence of high chloride levels.
Concrete	—Aesthetics —Less prone to vandalism	—Difficult to cast in one place leading to potential difficulties with cracks and leaks. —More expensive than self-supporting prefab towers.
Metal lined block and brick	—Aesthetics —Less prone to vandalism —Prefab air stripper insert eliminates problems associated with cast in place towers	—More expensive than self-supporting prefab towers.

no problems in this regard. Towers treating large quantities of heavily contaminated water may require tall stacks to direct the exhaust air up and away from the immediate area or more duct work to channel the off-gas to an air treatment device. This is more fully discussed in the section on air treatment.

Mist Eliminator System

Continuing downward, the next component encountered is the mist eliminator system, placed in the tower to prevent the discharge of large quantities of water entrained in the airstream. This is accomplished by forcing the airstream through a series of bends to impinge the water droplets on the surface of the mist eliminator. Mist eliminators come in two broad categories: chevron-type and pads. The chevron-type eliminators are made up of angled plates placed next to each other so that the air is forced to zigzag through, impinging the water on the plates. The chevron baffles are typically constructed of polyvinyl chloride (PVC), fiberglass-reinforced plastic (FRP), stainless steel, or aluminum. The baffles typically provide four to twelve direction changes as the air flows through. The deeper the baffle arrangement and the tighter the centerline distance between baffles, the better the mist elimination efficiency.

The pad-type mist eliminators are composed of filaments loosely bundled or woven into pads ranging from 3 to 12 inches thick. As the air flows through the pad, the water droplets are deposited on the filaments, which are usually made of polypropylene or stainless steel. The pad-type mist eliminators can provide greater mist removal, especially at higher airflow rates, but they have a higher pressure drop. In addition, the pad-type mist eliminators tend to be less expensive.

Water Distributor

Water is introduced into the tower through a water distributor, which ensures that the water is evenly distributed across the surface of the packing and the cross section of the tower, while allowing for smooth, unimpeded airflow upward to the top of the tower. The distributors fall into four general categories: (1) weir and trough arrangements, Figure 2-12; (2) header–lateral piping; (3) orifice pans, Figure 2-13; and (4) spray nozzles.

The weir and trough and header–lateral systems rely on the same basic concept: dividing the flow into successively smaller streams. The major drawback of these systems is the difficulty in assuring even

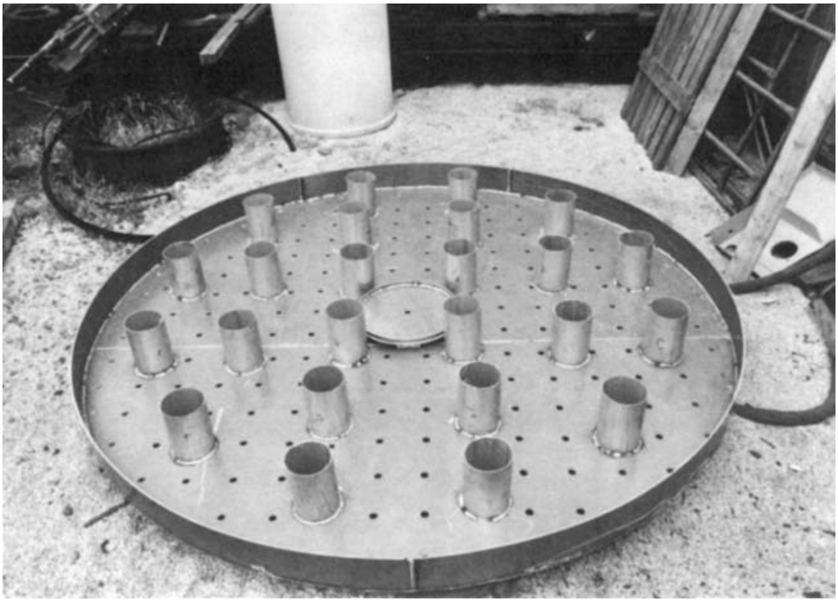

FIGURE 2-12. Weir and trough distributor.

water distribution, a factor that is critical to efficient tower operation. Weir systems have certain blind spots under the troughs where water does not fall, and header–lateral systems are notorious for unequal flow in different laterals, depending on their locations. However, these systems do find use where large airflows are required because they provide a large open area through which the air can pass. The weir and trough distributor has the unique advantage of providing mixing for large turndown ratios (the ratio of the maximum flow and the minimum flow that the tower will see). These distributors can be designed for turndowns as high as 7:1. Header–lateral units are typically not used in situations where variable flow (turndown ratios greater than 1:1) is expected. The turndown ratio becomes important for variable flow situations. When the groundwater is affected by rain and other outside influences, the flow from the wells may have to vary to maintain an adequate capture zone. The design of the treatment system, including all of its components, will have to include the possible variation in flow.

Orifice-type distributor trays avoid these problems of unequal distribution. The trays are designed to keep a standing head of water in them, thereby assuring that an equal pressure, and hence an equal flow, will be maintained at each orifice. Air stacks are provided to

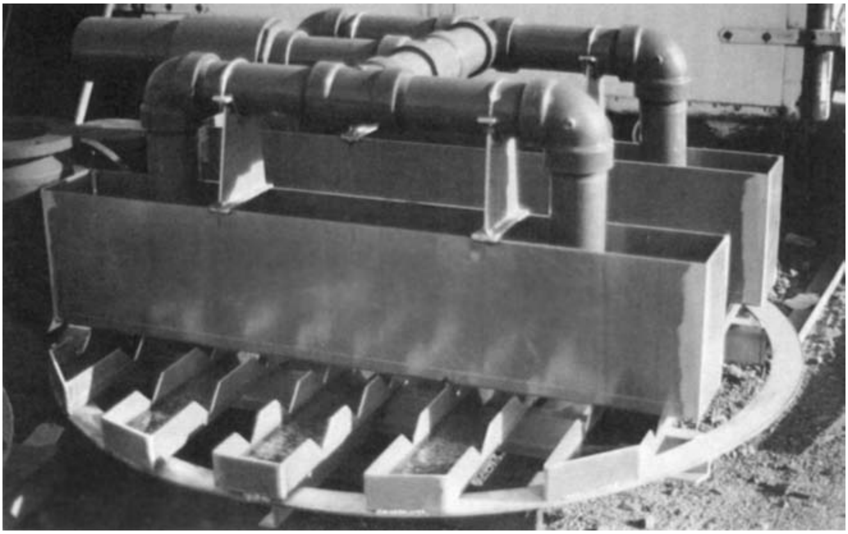

FIGURE 2-13. Orifice pan distributor.

allow gas flow through the tray. These trays do an effective job and are generally less expensive to fabricate than other distributor systems. The trays are typically designed to provide for turndown ratios as high as 3:1.

Spray nozzles are used most often in low-cost, off-the-shelf units. The major advantage of spray nozzles is that they immediately break up the water flow into droplets, thereby enhancing the mass transfer process. The major drawbacks are increased water pressure required to operate them, typically 2 to 5 pounds per square inch (psi), resulting in increased pumping costs; the extra tower space required to allow for their use; and clogging of the nozzle, especially in turbid waters. While spray nozzles can be designed for turndown ratios as high as 2:1, the operating cost associated with this capability is typically an additional 5 psi pressure loss.

Other Components

Several other components are involved in maintaining even air and water distribution in the tower. Throughout the depth of the packing are wall wipers and/or redistributors, which serve to rechannel any wall flow back toward the center of the column and ensure consistent distribution of air and water throughout the packed bed. Wall wiper rings should be provided at approximately 5-foot intervals. Redistributors, usually orifice pan or orifice plate distributors, should be provided at least every ten diameters of packed bed depth and sometimes as often as every six diameters. Thus, if a 25-foot bed is required in a 2-foot-diameter tower, at least one redistributor and possibly two should be provided.

Below the distributor lies the packing, which is supported by a packing support plate. We will finish discussing the structural components before moving on to the packing. The support plate must be structurally capable of supporting not only the weight of the packing but also the weight of any water present in the packed bed and any inorganic buildup that may collect on the packing over the life of the stripping unit. At the same time, the plate must have enough open area to deter flooding, a condition that results when the water flow downward through the tower is significantly impeded by the upward gas flow. When the water flow is restricted, a head of water builds up until the water's weight is enough to force its way through the plate. This leads to an unstable "burping" action, where first water and then air are alternately passed through the plate, decreasing removal efficiencies in the tower.

For most water treatment applications, FRP, stainless steel, aluminum, or polypropylene grating will provide adequate open area to prevent flooding, approximately 70 percent open area. In designs with very high liquid and gas loading rates, a gas-injection plate is sometimes used. These plates have a wavy appearance, which provides more open area than is possible with a flat plate by as much as 100 percent of the tower cross-sectional area. Air is "injected" through the sides of the undulations of the plate. These plates are usually fabricated from stainless steel and are more expensive than FRP grating.

Whether gratings or air-injection plates are used, the support tray must be held circumferentially and in many cases laterally. This support takes the form of a circumferential ring and structural channels or beams. Designing for a minimum $\frac{1}{4}$-inch plate deflection will usually ensure adequate strength and rigidity.

The design of the tower base will vary with system configuration; an integral clearwell may be supplied as part of the tower, or the water may flow by gravity to discharge into a surface water body or sewer. Whatever the configuration, it is imperative that a water seal be provided in the discharge line to prevent short circuiting of the tower due to air exiting via the discharge line. A hydraulic analysis of the discharge should also be performed to ensure that the water will not back up in the tower, possibly flooding the air blowers. Several common configurations are shown in Figure 2-14.

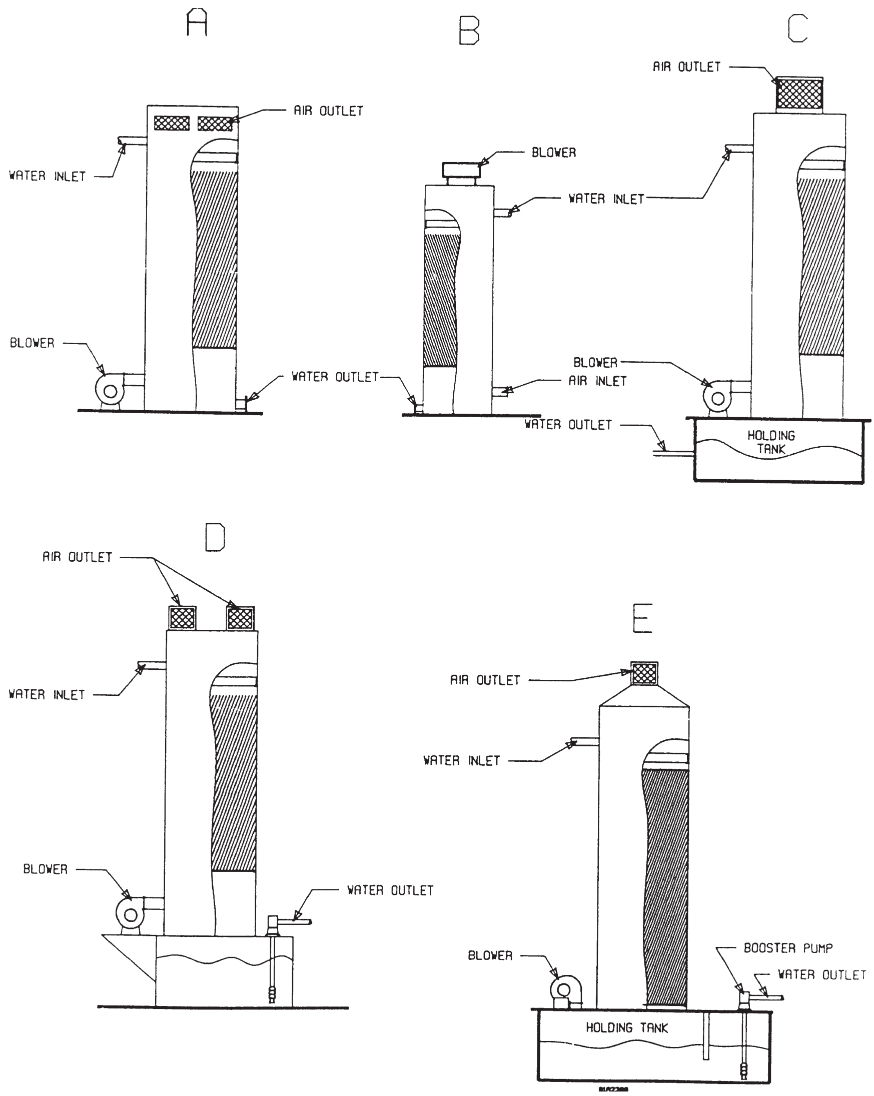

FIGURE 2-14. Common tower configurations: (A) integral basin with gravity discharge; (B) induced draft system with integral basin and gravity discharge; (C) below-grade storage basin and booster pump discharge; (D) above-grade integral booster pump basin; (E) low-profile below-grade basin with booster pump discharge.

Packing Material

The single most important component selection for the design engineer is the tower packing (Figure 2-15). The ideal tower packing will provide a large surface area for the air and water to interact and will also create turbulence in the water stream to constantly expose fresh water surfaces to the air. The packing should have a large void area to minimize the pressure drop through the tower. Additional considerations on packing choice include weight, corrosion resistance, the ability to maintain a uniform liquid flow, and, of course, price. Table 2-6 summarizes the basic properties of several representative packings. Because new packings are developed constantly, the reader should only use Table 2-6 as a guide and maintain a literature file on new packings.

Unfortunately, there is no single measure to determine the best tower packing. Measurements such as surface area per unit volume can be misleading because the surface area of the packing is not the same as the air/water interface area. Many of the packings with wide, sweeping surfaces may have only one side of their area wetted, essentially wasting the dry half. Other packings, because of their configurations, may cause channeling of the water, reducing the air/water contact area. For this reason, comparison pilot-scale tests using various packings are the only valid method of evaluation.

Another concern with respect to selecting the size and type of packing is the possibility of iron, calcium, and manganese precipitates forming on the packing material after extended operating periods. Precipitates

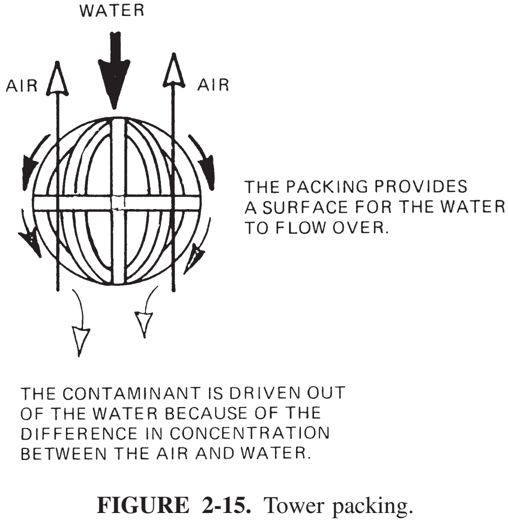

FIGURE 2-15. Tower packing.

TABLE 2-6 Characteristics of Several Polypropylene Packings

Packing*	Nominal Size	Weight lbs/ft^3	Surface ft^2/ft^3	Free Vol %	Packing Factor per ft
Tripacks	1″	6.2	85	90	28
Tripacks	2″	4.2	48	93	16
Tripacks	3.5″	3.3	38	95	14
Berl Saddles (ceramic)†	1″	45	79	69	NA
Pall Rings	2″	3.85	33	92	25
Novalox-Saddles	1″	5.2	78	81	33
Tellerettes (No. 3 Typol)	3.75″	4.7	30	92	NA
Hi-Flows	2″	3.7	33.5	94	NA
Lampacs	3.5″	4.2	45	93	14
Munters 12060 Structural	—	NA	68	95	27.4

NA = Not Available.

*Registered trademarks. Source: Manufacturer's literature.

†Source: *Chemical Engineer's Handbook*, 4th edition.

formation will reduce removal efficiencies and cause higher gas pressure drops. To minimize precipitation problems, larger packing sizes are recommended. Larger sizes will provide less surface area for precipitation, as well as larger spaces for airflow.

Advances in Packing Material

One of the great improvements in mass transfer technology has been the introduction of inexpensive plastic packings. The use of injection molding has allowed the creation of packings much more suited to the dual goals of maximum mass transfer surface and minimum pressure drop. Early packings, such as berl saddles and rashig rings, were limited to fairly simple shapes by the nature of their production process, usually in metals or ceramics. The packings shown in Figure 2-16 are all made of polypropylene, and their complex shapes assure a large void area to minimize pressure drop. Pilot testing of these packings have shown much better results than those obtained with the older packings. Polypropylene packing has several other benefits. It is chemically inert and will not degrade when exposed to most chemicals encountered in groundwater contamination. Extreme levels, greater than 1,000 ppm, of certain chlorinated compounds, particularly methylene chloride, can lead to a softening of the polypropylene and subsequent degradation of the mass transfer process. Polypropylene is very inexpensive; an equal volume of ceramic packing may cost eight to ten times as much. Finally, polypropylene is lightweight and strong, allowing greater packed bed depths without crushing the packing at the

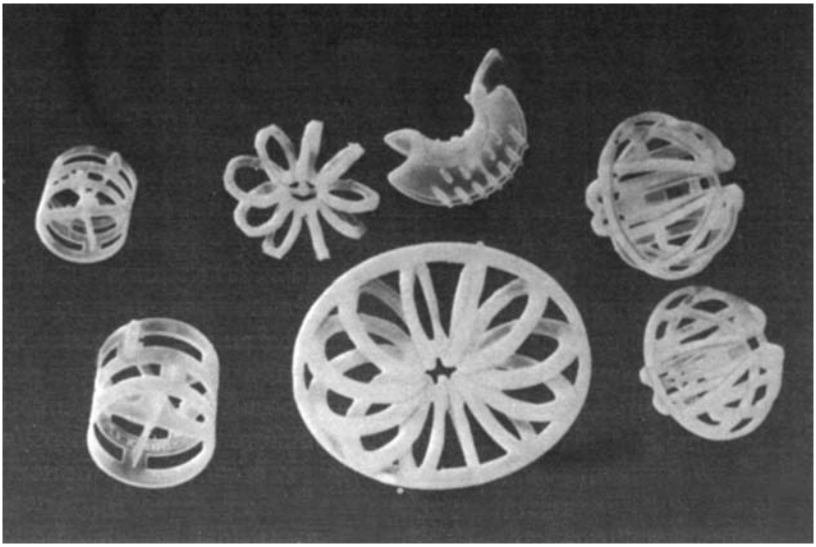

FIGURE 2-16. Examples of plastic tower packing. (Courtesy of Hydro Group.)

base of the tower. This strength also allows the packing to be dumped into a tower without damage; ceramic packing must be loaded into a tower filled with water to cushion its fall. Designing a tower to withstand such hydraulic loading adds to the cost of installation.

In situations where polypropylene is not appropriate, more resilient plastics such as Kynan or Teflon are available, but at prices fourteen to forty times that of polypropylene. Stainless-steel packings offer a more cost-effective alternative to Kynan or Teflon in most extreme situations, although packings made of stainless-steel material are generally less efficient than their plastic counterparts.

The packings shown in Figure 2-16 all fall into one general category: the randomly dumped packings. These packings are simply dumped into the tower and allowed to rest in whatever configuration they land. The other broad category of tower packing is the structured packings. These packings are physically stacked in the tower and configured to assure even water redistribution. These packings are not generally used in packed-column air stripping because of their high capital cost, the additional labor cost for their installation, and their fairly poor mass transfer efficiency. They exhibit lower head-loss characteristics, thus higher air-to-water ratios are achievable for the same power cost. Claims of superior fouling resistance have been made, but these claims have not been verified in field operations.

Air Delivery System

The final component of an air-stripping system is the air delivery system. Usually a forced draft blower is provided at the base of the tower, or housed nearby in a building if sound levels are a concern. However, with proper tower design, selection of a minimum air-to-water ratio, and minimization of the fan speed, the size and noise level of a blower can be kept to a minimum. Sound mufflers are available for insertion over the air inlet if desired, but these result in an increased pressure drop and only marginal reduction of the noise level. On some potable water installations, air filters are required to ensure no air particulates contact the water. These filters also serve as excellent sound mufflers. A complete packed tower is shown in Figure 2-17.

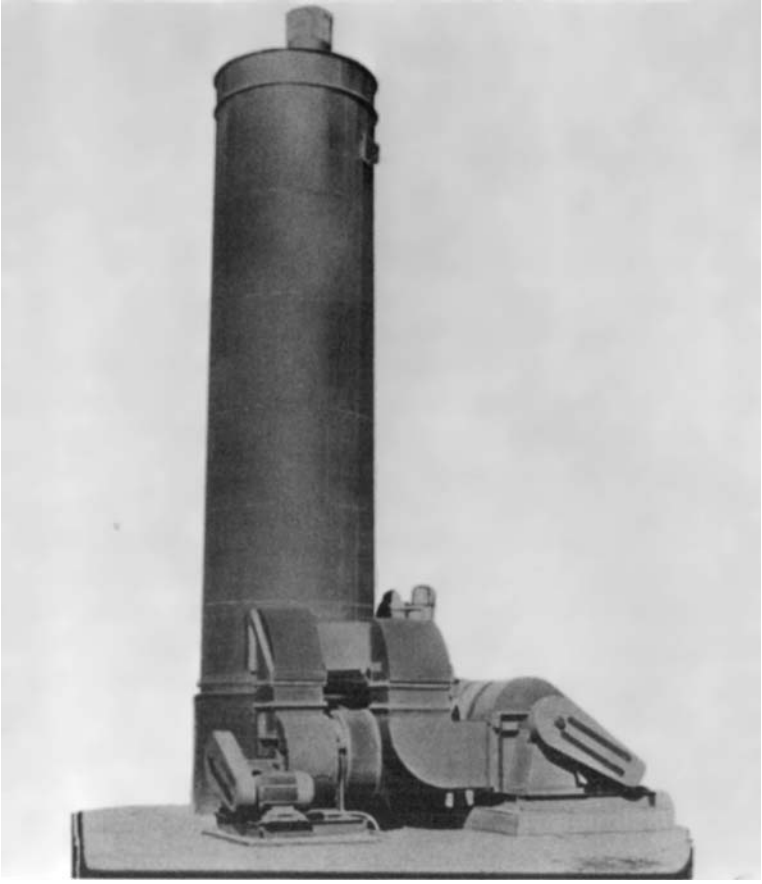

FIGURE 2-17. Example of a packed-tower air stripper. (Courtesy of Hydro Group.)

The alternative to a forced draft tower is an induced draft system where air is drawn through the tower by the blower. The blower may be mounted atop the tower or at the base. Induced draft units with blowers mounted on top are limited to somewhat lower pressure drops. Base-mounted induced draft systems often find application where the gases being discharged undergo further treatment before their release; i.e., carbon adsorption or incineration.

OPERATION AND MAINTENANCE

When installed, the operation of an air stripper can be a very simple matter. The air delivery system is controlled by the water supply pump(s) so that before water is introduced to the tower the blowers are activated. Because the only moving part is the blower, maintenance of the mechanical system is fairly straightforward. Thus, maintenance can be minimal, requiring only periodic inspection of the packing. However, under some circumstances, maintenance can be a major consideration in tower operation. There are several areas that can increase the required maintenance.

Overall system maintenance will vary depending on construction materials, environmental conditions, and water quality. The use of carbon steel, for instance, will require regular recoating to maintain the carbon steel shell or tower internals. FRP must also be maintained by recoating any exposed FRP components to prevent UV degradation.

Leaves and snow have been reported to clog air intake structures, and improperly designed systems have led to frozen piping. Freezing can be avoided by designing the tower and internals to be entirely self-draining, avoiding any interior ledges or pockets that could develop more than a thin coating of ice. Inlet and outlet piping should be provided with normally open solenoids that are heat traced and insulated to allow drainage of exposed piping upon shutdown. During normal operation, freezing is not a problem within the air-stripping tower except where the inlet water temperature drops below 35°F or in extremely cold climates (Alaska, for example). In these cases, temperature influences both the rate of mass transfer and Henry's law constant, thus impacting equipment and tower performance.

Water Quality Considerations

Certain inorganic water quality parameters pose operation and maintenance concerns when the use of packed-column aeration systems is being considered. Of particular note are the effects of dissolved iron, suspended solids, high microbial populations (degradable organics), and hardness.

During the aeration process, dissolved metals such as iron and manganese are oxidized. In most situations, the pH of the water is such that manganese deposition is not a problem; however, the transformation of ferrous iron to ferric iron is a real and often destructive problem in air-stripping operations. The oxidized iron is deposited on the packing material and in time causes a buildup that will bridge and clog the packed bed, leading to a decline in system efficiency. The degree to which iron deposition affects system performance is directly related to the level of dissolved iron in the water and other water quality characteristics such as pH and dissolved solids.

Iron deposition is probably the most underestimated problem with groundwater treatment systems in general and air strippers specifically. The problem starts when iron is not considered a contaminant and is not included in the analyses during the remedial investigation. The design engineer needs the concentration of iron, manganese, hardness, and other inorganic constituents in the water to correctly design an air stripper. Depending on the iron (Fe) concentration, the packing may have to be cleaned as often as every month. As a very rough rule of thumb, the following guidelines can be used:

<1 mg/L Fe	Low maintenance
2 to 5 mg/L Fe	Clean tower every three to six months
>10 mg/L Fe	Clean tower every one to two months

All of these values are also affected by temperature, pH, manganese, hardness, and other environmental factors. For example, the lower the pH, the slower the iron oxidation reaction. If the pH of the groundwater is 4.5 or 5.0, then iron precipitation will be greatly reduced as a maintenance problem. These concentration ranges should only be used as a rough guideline.

Pretreatment Considerations

The added cost of maintenance and the lower removal efficiency because of fouling may be sufficient to force pretreatment or the selection of alternative air-stripper designs. Pretreatment systems can cost as much if not more than the actual air stripper. The iron itself is easy to remove from water. Iron deposition can be controlled through the application of pretreatment technologies such as aeration/filtration and chemical sequestering. The effectiveness of any control technology will be related to the level of iron present.

Where oxygen is a problem in the tower, it can also be used as an opportunity to easily remove the iron from water. If the groundwater is aerated prior to discharge to the air stripper, then the iron will come out of solution and form insoluble iron hydroxide. This reaction occurs at a neutral pH (see Chapter 5 for detailed information on iron solubility at different pHs).

When the iron is in solid form, then the problem is solids/liquid separation. The iron particles are removed from water by a clarifier or filter. Usually, the suspended solids concentration is low enough for a filter to be used. After the solids have been removed, the groundwater can continue to the packed tower. The solids require more processing. Basically, the solids must be reduced to as small a volume as possible for final disposal (probably in a landfill). The solids will have to be sent to a thickener and then to some type of dewatering device (filter press, belt press, etc.).

As can be seen, several unit operations are required to remove the iron from the water. There are added capital costs for all of the extra units, and the operation cost will increase for chemicals, manpower, electricity, and sludge disposal. On large-scale systems, these costs will probably be more than the air stripper. On a small-scale system, the design engineer will probably find the costs for pretreatment prohibitive and switch to a different air stripper design. For example, a diffused aeration stripper can be used with high iron concentrations with no adverse effect from the iron.

The presence of high populations of microbial bacteria and/or high concentrations of degradable organics can lead to a biological buildup within the packed bed. This problem occurs because the packing material and highly oxygenated water offer an excellent environment for microbial growth. As with oxidized iron, a biological buildup can lead to a deterioration of system performance. Biological buildups are relatively uncommon in packed-column systems treating groundwater for municipal drinking water applications. The problem occurs more often in situations involving groundwater cleanups of petroleum spills, landfill leachate treatment, or anytime there are higher (>10 mg/L) concentrations of degradable organics. This problem is controlled through the use of chlorine (or other oxidizing agent) solutions generally added prior to the air stripper on an intermittent or constant basis. One note of caution when adding oxidizing agents to packed towers: The oxidizing agents can also increase the rate of oxidation of the inorganic constituents of the groundwater. For example, solving a biological buildup with chlorine oxidation can cause manganese to precipitate when it normally stays in solution.

One solution to bacteria buildup is to pretreat with a biological treatment unit. The biological unit can remove the degradable organics, and then the air stripper can remove the nondegradable organics. Low-concentration biological treatment designs are discussed in a later chapter.

Calcium hardness is another operation/maintenance consideration. In the air-stripping process, the potential for destabilization of the water is increased as a result of the removal of dissolved carbon dioxide from the water. The removal of carbon dioxide can lead to calcium carbonate deposition within the packed tower and in any post-treatment distribution system. If the destabilization is sufficient and occurs over a long enough period of time, the packing will become clogged with calcium carbonate. The problem can be controlled by minimizing the air-to-water ratio as much as possible (thus minimizing the stripping of carbon dioxide), or through the use of pretreatment. Pretreatment can take the form of softening systems or chemical sequestering agents.

More packed-tower air strippers have failed because of maintenance problems than because of poor designs. While most of this section has covered the details of the packed-tower design, the real world requires a complete understanding of the environmental factors that will affect the packing and subsequent operation of the tower.

Packing Cleaning Considerations

Plastic packing can be removed periodically and put into a tumbler so that the precipitate can be broken off. This method is labor intensive. Another option is acid wash, but acid treatment dramatically deteriorates the plastic packing, making it very fragile, and the approach not recommended. In some instances, conditioning chemicals may need to be added to the cleaning process because precipitates can form within weeks in hard water. In addition, handling and disposal of waste streams (cleaning fluids) will increase operational cost to the project, which can limit the.applicability of this technology.

Air Treatment

One of the major concerns surrounding air stripping is the discharge of VOCs to the atmosphere. The contamination is not destroyed in a mass transfer process; it is merely transported into another media. Two factors mitigate the effects of these atmospheric discharges: the first is the dilution that takes place in the tower before the vapors are emitted. Air-to-water ratios commonly used range from 25:1 to 250:1. Thus, the contaminant is diluted by a similar factor when it is transferred into the air. On top of this dilution, there is a natural dilution that occurs as soon as the airstream is dispersed into the atmosphere.

The second factor is that many compounds, such as trichloroethene and tetrachloroethene, will break down in the atmosphere under the effects of the sun's natural radiation. Trichloroethene, for example, has a half-life of approximately a day and a half in the atmosphere. The history of environmental treatment in the United States, however, has been toward destruction or final disposal, not switching the contaminant from one medium to another. Most states require that air discharges from stripping towers be treated before being released to the atmosphere.

In these states and in circumstances where the total discharge to the atmosphere is too high, the exhaust gases are usually treated using one of these means: activated carbon, incineration, or chemical destruction. The first two methods have proven to be the most viable approaches readily available in the marketplace.

Activated Carbon

By far the most common control technology applied to air strippers is vapor-phase granular activated carbon (VPGAC). The adsorption process in the vapor state is similar to the process as it occurs in the liquid phase (see the Carbon Adsorption section in this chapter), the major difference being the fluid treated. Detailed discussions of the adsorption mechanism and its application to air-stripper off-gas treatment are offered in several of the listed references.[15–17]

At first glance, vapor-phase carbon appears superfluous because liquid-phase carbon could treat the water directly. However, this system may save on carbon costs because the mass transfer in vapor-phase carbon is much faster; thus, smaller beds can be used and carbon usage decreases. In addition, the pore-size distribution in granular activated carbon (GAC) manufactured specifically for vapor-phase treatment allows for more of the surface area to be used for adsorption and a greater capacity for adsorption of chemicals in the vapor phase as compared to the liquid phase. There will also be fewer chemicals in the vapor stream competing for the available pore space because nonvolatile compounds, if present, will remain in the liquid phase.

Applications

VPGAC can be employed in systems that provide for off-site disposal or regeneration of the activated carbon or in systems that utilize on-site regeneration facilities. The nonregenerable systems are much more common in air-stripping applications because of the comparatively low capital cost associated with the technology and the relatively low levels of VOCs present in most air-stripping applications, see Figure 2-18. The biggest drawback of the nonregenerable systems is the need to remove, dispose of, and replace the VPGAC, typically as hazardous waste, on a regular basis. Several companies offer regeneration services on a commercial basis.

The typical regenerable VPGAC system has two modes of operation: adsorption and desorption. During the adsorption step, the air to be treated is passed through the activated carbon bed. There are many different types of bed configurations: thin bed, cartridge, and deep bed are common. The configuration is chosen based on the compounds treated and the design efficiency required.

Preheating of the air is almost always required with air-stripping operations. First, the design engineer must ensure that the water in the airstream does not come out of vapor phase and deposit on the carbon granules. Adsorption, considering both capacity and mass transfer,

FIGURE 2-18. Packed-tower air stripper with VPGAC.

improves substantially as relative humidity is lowered to about 40 percent, after which little improvement is gained (this also holds true in nonregenerable systems). Unlike nonregenerable VPGAC, after breakthrough has occurred, the carbon is not replaced. With a regenerable VPGAC process, the air treatment system is taken off-line and the carbon is regenerated in place. Often dual-column systems are designed to ensure that air treatment can continue even during the regeneration step. Because breakthrough will vary with the actual organic load, air humidity and temperature, and carbon age, timers are often used to take the VPGAC unit off-line on a regular basis.

The timing of the regeneration process may be changed as the system ages. Steam regeneration is much less rigorous than higher temperature regeneration; therefore, the actual, or “working,” capacity will be less for regenerated carbon, so cycle times will be much shorter than for a similarly sized nonregenerable VPGAC system (hot air will provide greater working capacities than steam).

Regeneration

Regenerable VPGAC processes rely on in-place regeneration of the activated carbon to reestablish at least part of the carbon’s adsorptive capacity. Regeneration occurs when adsorbed solute molecules are removed from the carbon surface through desorption in their original or a modified state with no change in the carbon surface. Steam is usually used for regeneration. Other means, such as hot gas, have become commercially available and can be combined with thermal oxidation of the hot regenerant gas to provide for complete organic contaminant destruction on-site.

The regeneration step consists of flowing steam in a countercurrent pattern through the carbon bed. The steam will desorb or remove the sorbed organic molecules from the carbon pores and carry them out of the carbon bed. This desorption process will typically last about an hour. All the steam used in the desorption process is run through a condenser. The condensate and free product resulting from the desorption process are collected. In some cases, the free product is then reused; in other cases, it is disposed. The aqueous condensate is saturated with the organics removed from the carbon. When the pure product is removed, the aqueous condensate may be recycled slowly back to the packed tower for blending and treatment with the normal influent. The aqueous condensate may need to be disposed of after a number of cycles if the concentration of the more soluble contaminants becomes too great to blend with the influent.

After the desorption step is complete, a cool-down period may follow, after which the regenerated unit is put back on-line. As the VPGAC is regenerated over and over again, it loses some of its original capacity. Generally, the expected life of the VPGAC is approximately five years before it must be replaced. VPGAC units running on single compounds will have longer carbon lives, but when the carbon is subjected to a mixture of organics, the carbon bed life can be reduced significantly.

Incineration

Incineration of the air-stripper off-gas is a second means of treatment. Incineration ideally converts compounds to carbon dioxide and water. Direct thermal incineration is sometimes used in air-stripping applications for landfills where methane flares are commonly in use; the stripper off gas is directed to the flares and incinerated at temperatures near 1,400°F. Other incinerators will run between 1,400 and 1,800°F. Flares can be elevated or can be enclosed at ground level and burned within the enclosure. The destruction of the contaminants is the major advantage of this technique over carbon adsorption, which serves only to concentrate the contaminants onto the carbon.

Catalytic Incinerators

Catalytic incineration utilizes a catalyst to enhance the destruction of the organic compounds, with very little heat loss. Therefore, a catalytic system can operate at reduced temperatures (600 to 900°F), significantly contributing to operating cost savings associated with fuel costs. Energy costs can be further reduced by reclaiming heat from the exhaust gases and using the exhaust to preheat the vapor stream.

Catalytic incinerators have been used to treat petroleum hydrocarbon because of the incinerator's sensitivity to contaminant characteristics and because of the operational conditions required for the incinerators. Catalysts are subject to poisoning and/or fouling by a variety of elements and chemical compounds, such as chlorinated compounds, sulfur, lead, mercury, iron oxides, and phosphorus. However, some catalysts are able to tolerate higher concentrations of these substances. Chromium oxide–aluminum oxide catalyst has been successfully used for the treatment of chlorinated hydrocarbons. Catalytic incinerators are not as commonly used as activated carbon, but the development of halogen-resistant catalysts has resulted in more widespread use.

Thermal Incinerators

The thermal incinerator for organic compound–air mixtures is a catalytic incinerator without the catalyst. This usually means that the incoming mixture must be heated to a temperature at which the organic compound will be oxidized. Most VOCs are reduced to desirable levels at exit gas temperatures of 1,500°F. However, thermal incineration is not appropriate for influent vapor streams containing high concentrations of chlorinated compounds. Partial or incomplete combustion of chlorinated compounds could result in the production of chlorine gas, dioxins, and other products of incomplete combustion.

All the air discharge control processes discussed above are commercially available in the United States from several equipment suppliers. The additions of the simplest air-treatment system will approximately double the capital cost of an air-stripping system. The use of on-site regeneration or incineration will increase the cost of treatment by as much as one to two dollars per thousand gallons treated. These are very general cost estimates that are strongly influenced by the degree of treatment required, the compounds and levels of organics present, the location of the site, and regulatory requirements.

Chemical Destruction

The objective of chemical destruction is to detoxify the waste stream by adding an oxidizing agent to chemically transform waste components. Organic molecules will be converted to carbon dioxide and water or to an intermediate product that may be less toxic than the original. Chemical oxidation of wastes is a well-established technology that is capable of destroying a wide range of organic compounds, such as chlorinated VOCs. The most common oxidizing agents used are ozone, hydrogen peroxide, and chlorine. Additionally, UV light is usually added, along with ozone and/or hydrogen peroxide, to accelerate the oxidation of chlorinated VOCs. Oxidizing agents are nonspecific and will react with any reducing agents present in the waste stream. Therefore, these processes are most economical when organics other than the constituents of concern are in low concentration.

ALTERNATIVE AIR-STRIPPING METHODS

A variety of aeration methods are available on the market today. Some are listed in Table 2-2. Of the technologies listed, packed columns have found the most widespread use. Other types of air-stripping and aeration processes include, but are not limited to, mechanical aerators and rotatory stripping.

Mechanical aerators typically used in water treatment are surface or submerged turbines or brushes. Surface aerators can be used in water treatment as an alternative to diffused aeration systems for stripping VOCs. The brushed-type aerator consists of several blades attached to a rotatory drum that is half submerged in water in the center of the tank. As the drum rotates, it disperses the water into the surrounding air, thereby providing interfacial contact between the air and the water for mass transfer to occur. The turbine-type aerator consists of a submerged propeller system located in the center of the tank and surrounded by a draft tube. As the submerged propeller rotates, it draws water from outside the draft tube through the inner section and into the air, providing contact between the air and water.

Another design for air stripping is the rotary stripper. In this unit, the water is passed through a chamber that is rotating at high speeds. The rotary stripper has found limited application in situations where a medium efficiency, low-profile system is required. The power costs associated with rotary strippers are extremely high compared to packed towers, making them an expensive alternative.

There are several miscellaneous stripping methods. The use of a cyclone aeration system, hollow fiber membrane air strippers,[18] hollow fiber membrane/oil stripping,[19] and hybrid processes are being explored as alternatives to packed-column aerators.

It is important to remember that there are other types of air strippers when designing a treatment system. The design engineer should not simply put a Band-Aid on a packed-tower design. Sometimes, the design engineer has to go back and start from the beginning. If maintenance is going to be a problem, alternative designs need to be evaluated.

Air stripping has become one of the workhorse technologies for the treatment of VOCs in groundwater. The combination of low cost, ease of operation, and the wide variety of compounds that can be removed from groundwater make stripping the first choice for many low concentration streams. Even in cases when the air discharge must be treated, air stripping is still often found to be the most cost-effective method.

Carbon Adsorption

The use of carbon for its adsorptive qualities has been known as early as 1550 BC when charcoal was utilized in the purification of medicines.

In the field of water treatment, both ancient Egyptians and 18th-century sailors utilized charcoal-lined vessels to provide for clean drinking water. The use of carbon as a water treatment process, though, traces its roots to London in the 1860s when some of the residents had their drinking water filtered through animal charcoal to remove tastes and color. Granular carbon filters were introduced in the 1930s for producing ultrapure water for the food and beverage industry. Following World War II, coal was utilized to produce high-activity, hard granular carbons on a commercial scale, leading to the widespread use that GAC has today.

The use of activated carbon to remove taste and odors from drinking water supplies is now an established technology. Since its introduction on a commercial scale, industry has also taken advantage of activated carbon's unique ability to adsorb a variety of organic compounds for product purification, water, and wastewater treatment. This variety of carbon is produced by subjecting a carbon source (e.g., nutshell, wood, coal) to physical and chemical processes known as *activation*. The process involves exposing the carbon source to high temperatures (600 to 900 degrees Celsius [°C]) in an inert atmosphere. Chemical activation involves impregnation of the carbon source with acids such as phosphoric acid or bases such as sodium or potassium hydroxide.

Based on its history and unique properties, activated carbon has now become a proven technology for the removal of synthetic organic contaminants from groundwater. Although these contaminants don't exhibit traditional taste and odor characteristics and may be present in trace-level concentrations rather than the high levels found in wastewaters, removal may be required because of toxicity concerns.

Forms of Activated Carbon

With advances in manufacturing technologies, activated carbon is available in many forms to suit various applications. Some of the commonly used forms of activated carbon are discussed below.

Granular Activated Carbon

This form is composed of irregular-shaped granules ranging in size from 0.2 to 0.5 millimeters (mm) and has wide-ranging liquid- and gas-phase applications. It is used extensively in the environmental industry to treat effluent gases and effluent groundwater from soil and groundwater remediation systems.

Powdered Activated Carbon

This form is composed of pulverized carbon with particle sizes less than 0.18 mm. It is mainly used in liquid-phase treatment and flue-gas treatment.

Extruded Activated Carbon

Activated carbon can be extruded to form cylindrical pellets of diameters ranging from 0.8 to 5 mm. Because of their high mechanical strength, low dust content, and low pressure drop, these cylindrical pellets are suited to gas-phase applications.

Carbon Cloth/Carbon Briquettes

Activated carbon can be impregnated onto certain varieties of cloth and fabrics or manufactured as briquettes to suit applications.

Concepts of Adsorption

Adsorption is a natural process in which molecules of a liquid or gas are attracted and then held at the surface of a solid. Physical adsorption refers to the attraction caused by the surface tension of a solid that causes molecules to be held at the surface of the solids. Chemical adsorption involves actual chemical bonding at the solid's surface. Physical adsorption is reversible if sufficient energy is added to overcome the attractive forces, while chemical adsorption is not a reversible reaction.

Adsorption on activated carbon is of a physical nature. What makes this material such an excellent adsorbent is the large degree of surface area contained within the carbon particle that is accessible for the adsorption process. The surface area of granular carbons ranges up to 1,400 square meters per gram of material. As the surface area of the activated carbon is internal to the material, crushing the granular material will not increase its surface area. Even in its crushed or powdered state, activated carbon still retains internal surface area, making it an effective adsorbent.

Two methods have been developed to describe the internal structure of the carbon particle. The original method used macropores and micropores as the basis of description. Figure 2-19 shows macropores (openings with diameters greater than 50 nanometers [nm]) where the organics are transported to the interior of the carbon particle, and micropores where most of the adsorption takes place.

Figure 2-20 is a micrograph of an actual carbon particle. In this picture, the carbon particle has transport pores, or openings, that allow

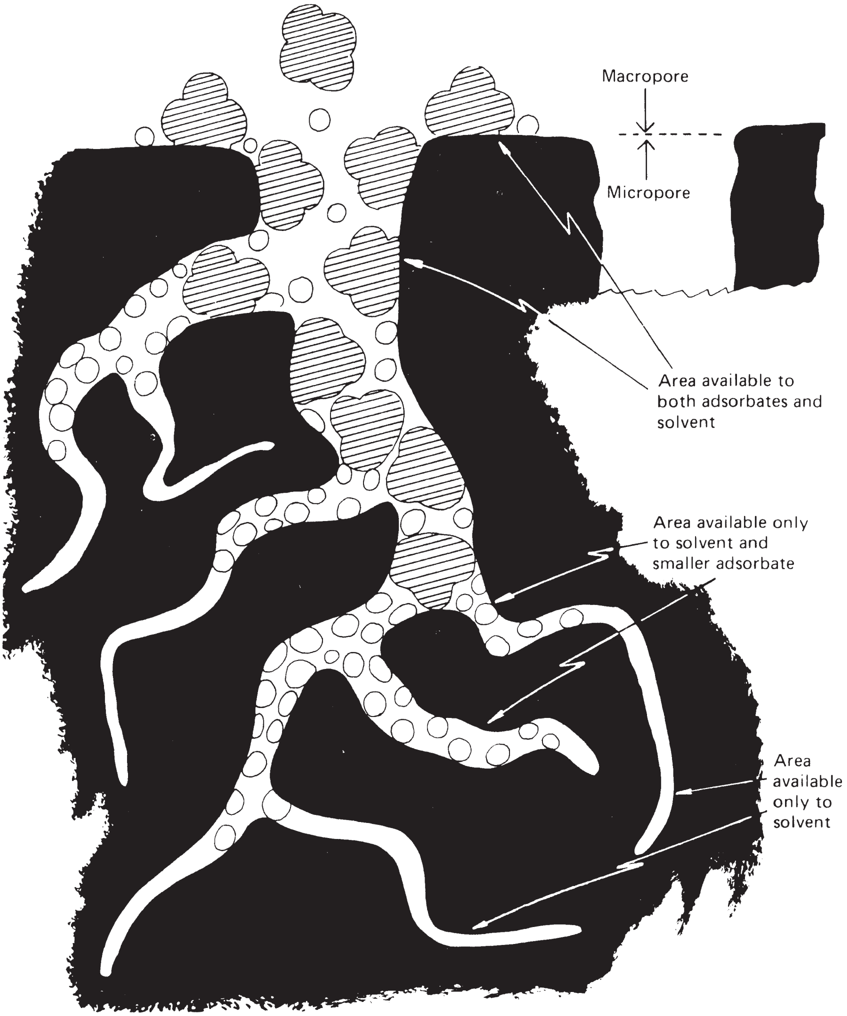

FIGURE 2-19. Internal structure of activated carbon.

the passage of the contaminant molecules and provide an entrance into the interior structure of the carbon particle. Although some adsorption may take place along these pores, they mainly serve to conduct the molecules to the *adsorption pores* where adsorption takes place. Many such adsorption pores are large enough to contain small molecules, so the effective surface area for adsorption of a particular species depends on its size and the available surface area of the pores it can enter.

In either case the capacity of a particular grade of carbon may vary for different species. Standard tests have been developed to identify

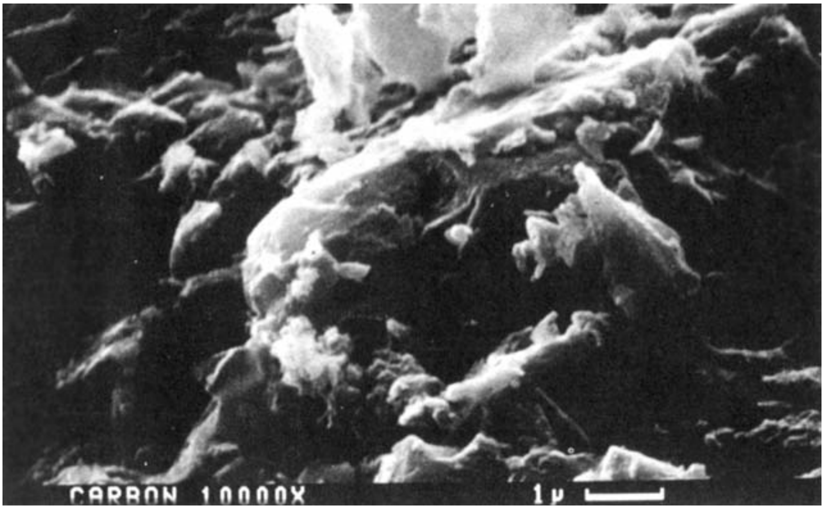

FIGURE 2-20. Micrograph of an activated carbon particle.

such capacities. These tests may utilize the iodine molecules to identify small pores and molasses to identify the larger pore structure, for example. There are a wide variety of activated carbons available, and properties such as surface area and pore-size distribution will determine their applicability to any given situation. These properties are described further below.

Properties of Activated Carbon

Iodine Number

The iodine number is the most fundamental parameter used to characterize adsorption capacity and activated carbon performance. It is a measure of the micropore content of carbon (0 to 2 nm). The iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon, and it approximates the internal surface area (square meters per gram).

Methylene Blue

Methylene blue is the measure of the mesopore (2 to 50 nm) structure of activated carbon.

Caramel dp (Molasses Number)

The molasses number is a guideline for measuring the capacity of carbon for large adsorbate molecules. It is the measure of the macropore (>50 nm) structure of activated carbon. Color pigments are generally large and cannot enter small pores; therefore, the number is used to quantify the degree of decolorization of a standard adsorbate (generally molasses solution).

Ash Content

Ash content quantifies the amount of impurities in the activated carbon. The impurities include the inorganic residue left after heating the raw material during manufacture. Common ash constituents include silica, alumina, iron, calcium, and magnesium. Ash content reduces the effectiveness of activated carbon.

Hardness and Abrasion Number

The hardness and abrasion number is a measure of the activated carbon's resistance to attrition. It is used to characterize various carbon types used in aqueous-phase applications. It indicates the ability of the activated carbon to withstand turbulence and frictional forces caused during handling and operation. Hardness of activated carbon depends on the raw material, manufacturing process, and activity level.

EVALUATION PROCEDURES—ADSORPTION ISOTHERMS

The adsorption mechanism consists of three steps: (1) diffusion of the molecules through the liquid phase to the carbon particle, (2) diffusion of the molecules through the transport pores (macropores) to the adsorption site, and (3) the adsorption of the molecule to the surface. The characteristics of the molecule will determine the rate of each step and finally the amount of time required for the entire adsorption process. Less soluble organics, for example, will diffuse rapidly to the granule, and large molecules will move slowly through the pore structure. Generally, the chlorinated solvents found to be contaminating groundwater are amenable to activated carbon adsorption because of their low solubility and small molecular size, enabling effective use of the adsorption area in smaller pores. However, it is important for each contamination problem to be properly evaluated.

The first step in evaluating activated carbon adsorption for a specific application is to assess its feasibility by using a liquid-phase adsorption isotherm test. An adsorption isotherm test is a batch test designed to demonstrate the degree to which a particular dissolved organic compound (adsorbate) is adsorbed on activated carbon (adsorbent). The data generated show the distribution of adsorbate between the adsorbent and solution phases at various adsorbate concentrations. From the data, a plot of the amount of impurity remaining in solution at constant temperature can be generated. For a single adsorbate, a straight line plot (on log–log paper) can be obtained when using the empirical Freundlich equation:

$$x/m = kc^{(1/n)} \text{ or } \log x/m = \log k + 1/n \log c \qquad (2\text{-}5)$$

where

x = the amount of contaminant adsorbed
m = weight of carbon
c = equilibrium concentration in solution after desorption
= k and n are constants

For mixtures of adsorbates, a series of straight lines can be obtained. The presence of a nonadsorbable component will result in a curvature of the line when in combination with an adsorbable component, and in a vertical line when alone.

Data for generating this type of isotherm are obtained by treating fixed volumes of the water sample with a series of known weights of carbon. The carbon–liquid mixture is agitated for a fixed time at a constant temperature. After the carbon has been removed by filtration, the residual adsorbate concentration is then determined. The amount of organic adsorbed by the carbon (x) is divided by the weight of carbon in the sample (m) to give one value of x/m for the isotherm. For contaminants that are volatile at ambient temperatures, the isotherm tests

TABLE 2-7 Carbon Adsorption Isotherm for Trichloroethene

m	*c*, TCE Remaining		*x*	
Carbon (g)	(ppm)	(mg)	TCE Adsorbed (mg)	*x/m*
Control	1.600	0.800	—	—
0.0005	1.490	0.745	0.055	110.0
0.0010	1.520	0.760	0.040	40.0
0.0025	1.290	0.645	0.155	62.0
0.0050	1.060	0.530	0.270	54.0
0.010	0.860	0.430	0.370	37.0
0.025	0.285	0.143	0.657	26.3
0.050	0.165	0.083	0.717	14.3
0.100	0.035	0.018	0.782	7.8
0.250	<0.010	—	0.800	—
0.500	<0.010	—	0.800	—

Conditions:
Type of carbon—Filtrasorb 300
Temperature—ambient
Sample volume—500 ml
Agitation time—4.0 hr

are conducted using water samples with no head space to prevent loss of contaminants to volatilization. To estimate the capacity of carbon for the contaminant then, one uses the x/m value that corresponds to its influent concentration C_0. This value (x/m) represents the maximum amount of contaminant adsorbed per unit weight of carbon when the carbon is in equilibrium with the untreated contaminant concentration.

Table 2-7 presents the isotherm data for trichloroethene at 1,600 μg/L. The data are summarized in Figure 2-21.

As an example, assume trichloroethene was present in groundwater at 200 μg/L. According to the isotherm, the equilibrium capacity is 19.5 mg trichloroethene adsorbed per gram of carbon, or a capacity of about 2 percent. Therefore, the amount of carbon required would be

$$(0.2 \text{ mg/L})/(19.5 \text{ mg/g}) = 0.01 \text{ gram carbon/liter of water}$$

or approximately 0.1 pounds per 1,000 gallons treated. This capacity is based on allowing the activated carbon to reach equilibrium

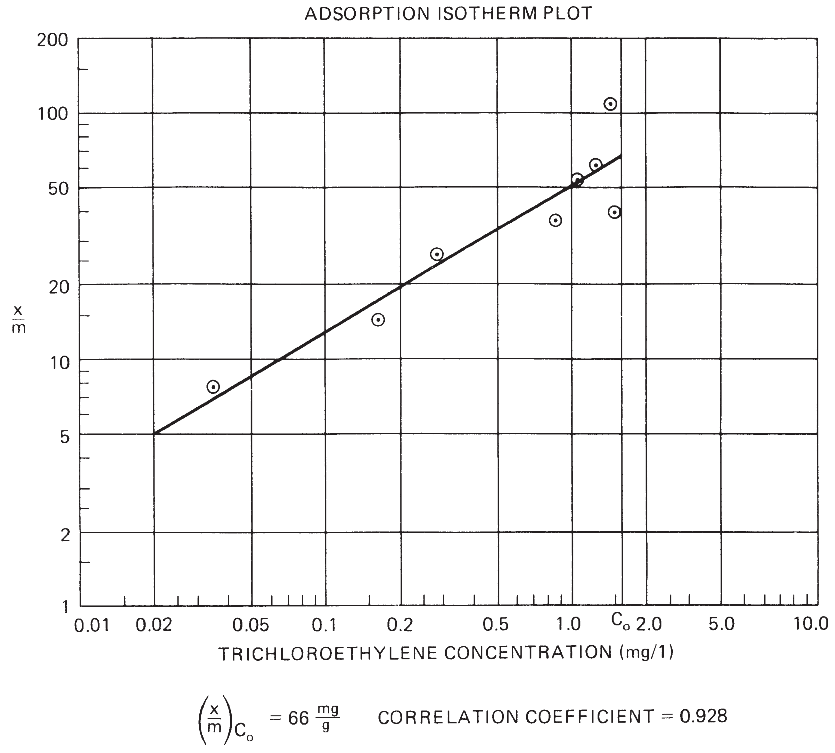

FIGURE 2-21. Trichloroethene adsorption isotherm plot.

TABLE 2-8 Adsorption Capacity for Specific Organic Compounds

	Compound	Adsorption Capacity (mg compound/g carbon) at 500 ppb	Reference
1	Acetone	43	1
2	Benzene	80	1
3	Bromodichloromethane	5	4
4	Bromoform	13.6	4
5	Carbon tetrachloride	6.2	2
6	Chlorobenzene	45	3
7	Chloroform	1.6	1
8	2-Chlorophenol	38	3
9	p-Dichlorobenzene (1,4)	87.3	4
10	1,1-Dichloroethane	1.2	4
11	1,2-Dichloroethane	2	2
12	1,1-Dichloroethylene	3.4	4
13	cis-1,2-Dichloroethylene	9	5
14	trans-1,2-Dichloroethylene	2.2	4
15	Ethylbenzene	18	1
16	Hexachlorobenzene	42	3
17	Methylene chloride	0.8	3
18	Methylethylketone	94	1
19	Methyl naphthalene	150	5
20	Methyl tert-butyl-ether	6.5	5
21	Naphthalene	5.6	3
22	Pentachlorophenol	100	3
23	Phenol	161	1
24	Tetrachloroethylene	34.5	2
25	Toluene	50	1
26	1,1,1-Trichloroethane	2	2
27	1,1,2-Trichloroethane	3.7	4
28	Trichloroethylene	18.2	2
29	Vinyl chloride	Trace	3
30	o-Xylene	75	4

1. Verschuren, Karel. *Handbook of Environmental Data on Organic Chemicals*. New York: Van Nostrand Reinhold, 1983.
2. Uhler, R. E., et al. *Treatment Alternatives for Groundwater Contamination*. James M. Montgomery, Consulting Engineers.
3. Stenzel, Mark. Letter of Correspondence to Evan Nyer, August 22, 1984.
4. USEPA, *Carbon Adsorption Isotherms for Toxic Organics*, EPA-600/8-80-023, Municipal Environmental Research Laboratory, April 1980.
5. Roy, Al. *Calgon Carbon*, (personal correspondance) 1991.

with trichloroethene, an ideal condition not usually obtainable in practice. But, the isotherm evaluation does prove that carbon adsorption is feasible and should be evaluated further.

Table 2-8 shows the equilibrium adsorption capacities of some typical groundwater contaminants (synthetic organic solvents and other compounds) as determined from isotherm testing.

EVALUATION PROCEDURES — DYNAMIC COLUMN STUDY

To design an activated carbon adsorption system, additional information that is not available from the adsorption isotherm must be obtained. The optimum operating capacity and contact time need to be established to determine the adsorber size and optimum system configuration. The optimum contact time and mass transfer zone depend on the rate at which the contaminant is adsorbed by the carbon and can be determined only by dynamic testing. In practice, it is often most cost-effective to engage carbon vendors who typically have spreadsheets and/or models used to calculate the optimum contact time and mass transfer zone for common compounds.

If a column test is required, the procedure involves a series of columns connected in series, as shown in Figure 2-22. Each column is filled with an amount of carbon calculated to provide superficial contact times of 15 to 60 minutes per column. The liquid rate to the column is usually in the range of 2 gpm/ft^2, although it may vary during the test, as at that point the contact time is more important. The surface-loading rate may be of more importance if there are suspended solids present and the activated carbon bed is to act as a filtering medium, as well as an adsorption process.

Water is pumped through the column system, and effluent samples are collected from each of the columns. The adsorption isotherm test should provide an estimate of how often testing should be done. The amount of the contaminant in the column effluent is plotted against the volume throughput of each column. The result is a series of curves, each representing a column. The successive curves also represent increasing contact times in a single bed. Figure 2-23 shows an example of a column study where each column represents 15 minutes of contact time. The curves obtained are termed breakthrough curves as they represent the concentration or amount of contaminants present in the effluent (which have passed through the column unabsorbed).

The results of a dynamic column study are utilized to establish the design of an operating carbon adsorption system. The first step is to establish the contact time required in the operating system. For each of the breakthrough curves established in the column study, a carbon usage rate can be calculated. This usage rate is the pounds of carbon required for a given volume of liquid to maintain the contaminant at a desired level in the effluent. The usage rate is calculated by dividing the amount of carbon on-line by the volume of water treated when the desired effluent concentration is exceeded, or the breakpoint of the breakthrough curve. The carbon usage rates can then be plotted for

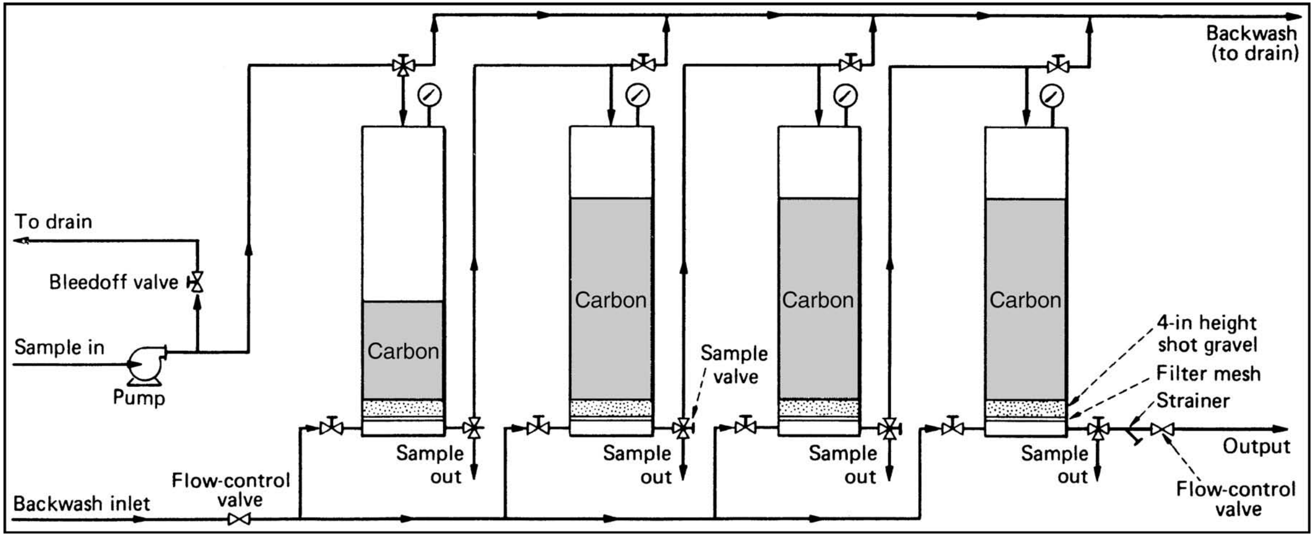

FIGURE 2-22. Laboratory series column adsorption test.

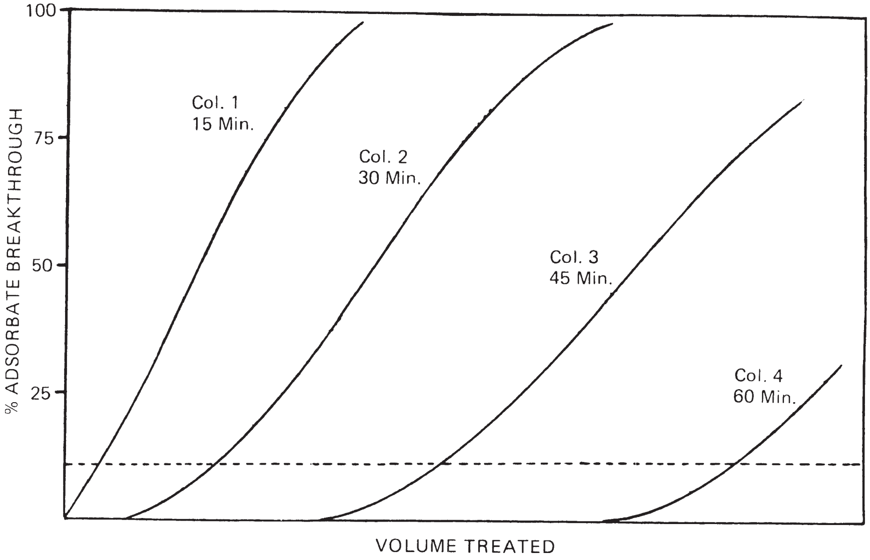

FIGURE 2-23. Column study results: breakthrough curves.

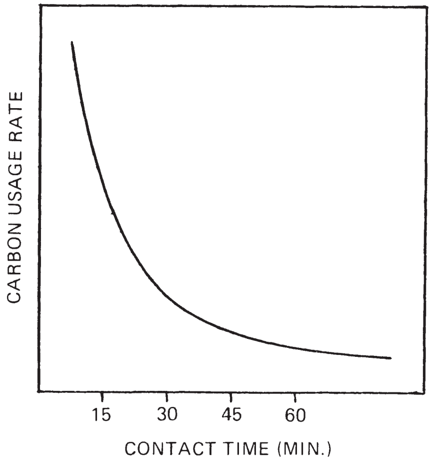

FIGURE 2-24. Optimum carbon contact time.

each contact time (column) as shown in Figure 2-24, and the optimum contact time determined as the point at which increasing contact time obtains little improvement in carbon usage. The amount of carbon on-line is then established by multiplying the contact time by the flow rate to obtain the volume of the carbon bed.

The next step is to consider whether only a single carbon adsorber is required or if a second unit in series would yield substantial benefits. Figure 2-25 shows the configuration of two breakthrough curves. The steep curve indicates a relatively short mass transfer zone. In this case, good utilization of the activated carbon can be realized in a single bed where the carbon is exchanged when the effluent concentration exceeds the desired level. The gradually sloping curve indicates a long mass transfer zone. For these instances, a staged system would provide more optimum usage. A second stage will maintain final effluent quality while the effluent from the first step gradually rises to near influent concentrations, utilizing all of the adsorptive capacity of the carbon. When the carbon in the first unit is fully utilized, it is then replaced with fresh carbon and put back on-line as the final stage, allowing full utilization of the carbon in the other unit now in service as the first stage. The concept of staged adsorbers is of particular value when considering water that contains a variety of contaminants exhibiting differing adsorbities requires treatment.

After the contact time has been established and the evaluation of the breakthrough curves has indicated whether a single bed or staged system is preferred, the design engineer can select the adsorber configuration. If the breakthrough curve is steep, usually in the case of single or similar contaminants, the single fixed-bed downflow adsorber is the most economical choice. The contact time will establish the

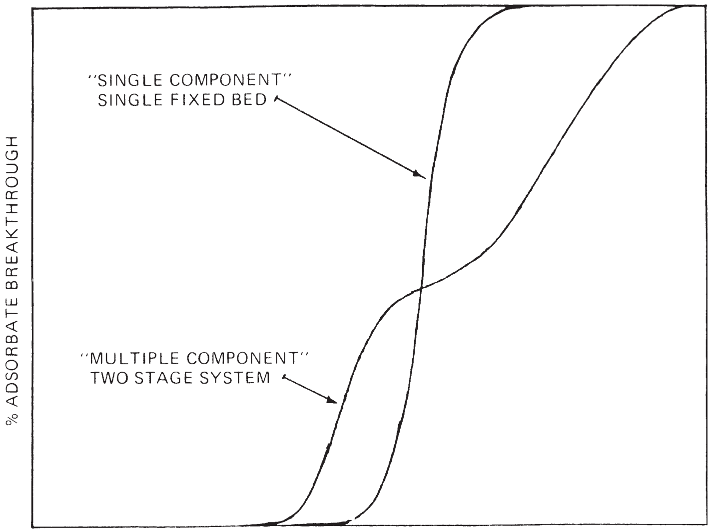

FIGURE 2-25. Mass transfer zones for two typical breakthrough curves.

total carbon volume as noted above. By weighing considerations such as flow and carbon volume, the design engineer will select the vessel size and whether multiple units (operated in parallel) may be required.

The simplest downflow fixed bed is the gravity adsorber. Because the downflow unit operates as a filter and is not a pressure vessel, flow is limited to 2 gpm/ft^2. At 2 gpm/ft^2, the typical carbon depth is 4 feet, yielding a contact time of 15 minutes. The effluent from a gravity adsorber will require pumping if needed for a pressure water system. Because the system depends on gravity as the motive force, the gravity adsorber may require backwashing if suspended solids are present in the influent.

The fixed-bed system can also be contained in a pressure vessel. This vessel allows greater bed depth and higher surface loading rates (up to 5 gpm/ft^2) or greater contact times. This system can also be operated at higher pressures so the unit could be placed inline between the pump and downstream usage. The pressure drop through a typical granular carbon bed is provided in Figure 2-26.

If the breakthrough curve is gradual or discontinuous (has a temporary plateau value) because of multiple contaminants, the design engineer may wish to specify a staged carbon adsorption system to obtain more optimum utilization of the adsorptive capacity of the carbon. The simplest staged adsorption system is two single fixed beds in series. If the mass transfer zone can be maintained within a single bed, then the second stage will be able to maintain effluent quality, while the carbon in the first stage is obtaining full use of its adsorptive capacity. When the carbon in the first stage is fully utilized, it is exchanged with fresh carbon and returned to service as the second stage. The fixed-bed downflow system has the added advantage of operating as a media filter with elimination of suspended solids in the effluent.

Another form of the staged bed system is the upflow moving bed design. This system may be of use when long contact times are required, and the breakthrough curve indicates that even a two-stage system is insufficient to provide economical use of the carbon.

In this process, the carbon is placed in a large cone-bottomed vessel. The cone bottom is desirable because the carbon removed will be of the mass (plug) flow variety, in which the material at the side walls will move downward in the vessel at the same rate as the material in the center. Flow from the center only is termed rat-holing, which results in the uneven distribution of fresh and partially spent carbon in the bed and may cause premature breakthrough.

The water flow is directed up through the bed at rates to 8 gpm/ft^2. At this rate, there may be a slight expansion of the bed. This will

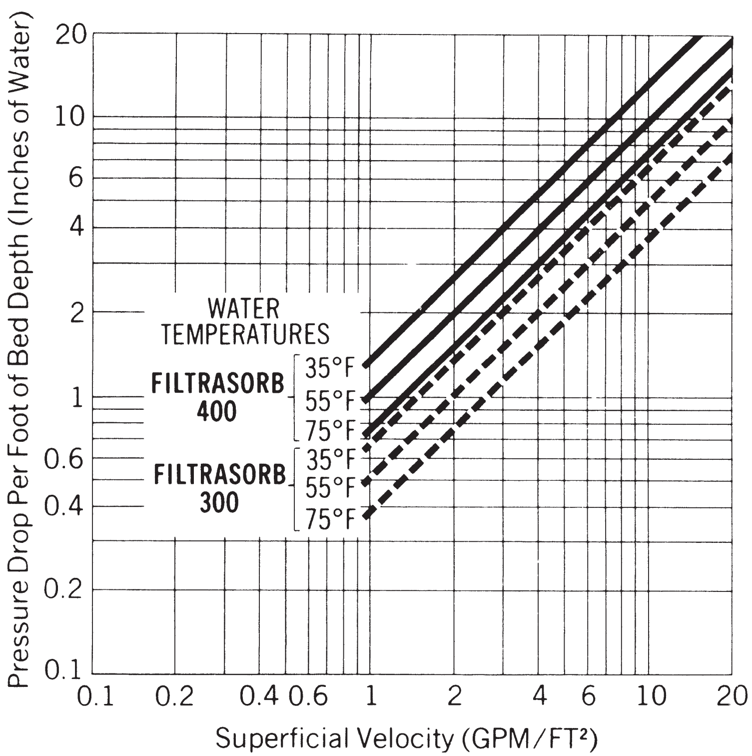

FIGURE 2-26. Downflow pressure drop through a backwashed segregated bed of Filtersorb 300 and Filtersorb 400. (Courtesy of Calgon Carbon Corp.)

produce a small amount of carbon fines material in the effluent, which, if a problem, will require nominal filtration.

When a portion of the carbon is fully utilized, it is withdrawn from the bottom of the unit, and an equal volume of fresh carbon is placed at the top of the bed. The portion of the bed requiring replacement may be anywhere from 5 to 50 percent, depending on the breakthrough curve. Replacement volumes of 50 percent or greater usually indicate that a two-staged fixed-bed system may be a better selection. It is very unusual to find an upflow carbon adsorber used in groundwater cleanups.

GRANULAR ACTIVATED CARBON REPLACEMENT CONSIDERATIONS

The supply of GAC to the adsorption system may be a significant operating cost factor. Usually, the usage rate in a groundwater treatment system is not at a level that would justify the consideration of an on-site regeneration facility. The most common form of replacement is to recharge the unit with fresh activated carbon, which can be virgin carbon or reactivated carbon with the reactivation occurring off-site.

As is often the case in groundwater treatment, the contaminant may be a volatile organic solvent. If no nonvolatile contaminants are present, recent studies have shown that much of the adsorptive capacity may be recovered by regenerating the carbon in place, or in situ. This can be accomplished in a fixed bed by withholding the unit from the process and passing steam through the bed. Regeneration in a moving bed can be affected by removing the carbon from the bed, exposing it to steam in a separate unit, and utilizing the regenerated material as fresh material at the top of the bed. Depending on the process, carbon can be utilized from five to ten times before its capacity degenerates to an ineffective level. The condensation and treatment of the steam used in the regeneration step needs to be addressed as a separate operation. This regenerative technique has a better chance of success if there is a single contaminant in the water.

As noted above, one carbon replacement option is to have the spent material thermally reactivated off-site. Spent carbon is transported in Department of Transportation (DOT)-approved containers and trailers. Following inspection and acceptance, the spent carbon is stored in slurry form in storage tanks. After dewatering, the carbon is fed into furnaces where it is heated at progressively higher temperatures (up to 1,800°F) to remove moisture, VOCs, and carbonized char. Most of the VOCs are destroyed in the furnace. The remaining contaminants are thermally oxidized in an afterburner that has organics removal efficiencies of 99.99 percent. The carbon is then passed through venturi scrubbers to remove particulates and packed-bed caustic scrubbers to remove acid gases. A wet electrostatic precipitator is used to remove the remaining particulates.

The advantage of regeneration is the recovery of the GAC for further use. The regeneration step may be a custom operation in which the spent carbon is regenerated as a batch and returned to the user. Regeneration may incur a 10- to 20-percent material loss, which must be made up to maintain the same amount of carbon on-line. Pool regeneration involves the collection and regeneration of many small carbon units to effect economy of scale, but the carbon returned is not the original material. The energy required to regenerate spent carbon is less compared to the manufacture of an equal quantity of virgin carbon. In addition, facilities can earn environmental credits for regenerating spent activated carbon.

Virgin carbon should be used in applications involving the treatment of water for reuse (potable applications, for example), but reactivated carbon is generally less expensive in applications involving aquifer restoration where the water is treated for discharge.

Many groundwater applications require only small amounts of activated carbon. The “55-gallon” drum design is widely used in groundwater treatment systems. While the sizes vary, it normally requires a minimum of 1,000 pounds of carbon to 2,000 pounds of carbon for the carbon company to economically pick up and regenerate the spent carbon. Therefore, smaller units cannot take advantage of a regeneration service as part of the purchase of activated carbon.

There are three choices for carbon disposal when using the small units: (1) stockpile and regenerate, (2) landfill, or (3) incineration. The first choice is to accumulate enough carbon to send to a regeneration facility. This can be done by combining spent carbon from one or more remediation sites. The main problem with this scenario is that the spent carbon can be considered a hazardous waste and could fall under regulations for hazardous waste storage. Even when the several locations combine to regenerate their carbon, each individual carbon canister will have to be analyzed before regeneration. The carbon regeneration companies need this information to ensure that there are no compounds present that will not be destroyed or captured by their regeneration system. The detailed analysis will add significant increases to the cost of the regeneration of small volumes.

The second method for disposal is to place the spent carbon in a landfill. Once again, analysis will have to be performed on each drum of spent carbon. In this case, the tests are needed to ensure that the spent carbon will meet all regulations concerning solid waste placed in a hazardous waste landfill. The land disposal restrictions may significantly limit options for landfilling spent carbon.

A second problem with placing spent carbon in a landfill is the nature of the adsorption process. As we discussed at the beginning of this section, carbon adsorption is an equilibrium process. Carbon isotherms are based on the concentration in equilibrium between the carbon and the water. If the spent carbon comes into contact with clean water, equilibrium will be established and some of the material will be exchanged to the water. Therefore, a landfill is not a good long-term solution for disposal of spent activated carbon.

The third method for disposal is incineration. In this case, both the carbon and the hazardous waste are destroyed. While this solution can be expensive, small quantities may be economical, and future liabilities are eliminated.

OPERATING RESULTS—CASE STUDIES

GAC has been used successfully in many cases to treat contaminated groundwater. The case studies presented here show some of the wide variety of organic compounds and concentrations that may be present in groundwater that can be removed effectively and economically by granular carbon adsorption.

Table 2-9 summarizes actual cases in which carbon was used to treat contaminated groundwater for drinking water use. All of these cases used virgin-grade GAC to ensure the purity of the water.

This review shows that in cases where one contaminant is present in substantial quantity, effective use of the carbon can be obtained with short contact times (less than thirty minutes) and a single fixed-bed system. This design provides for minimal equipment and carbon on-line and subsequently minimum treatment cost. In a vast majority of cases involving contaminant concentrations at micrograms-per-liter levels, carbon usage rates are less than 0.5 pounds per 1,000 gallons.

If carbon treatment is being used for drinking water purposes, chlorination is usually used after the adsorption process to ensure no biological activity in the downstream distribution system. Table 2-10 provides cases of groundwater contamination in which contaminants are present at milligrams-per-liter levels. These examples include cases in which chemical spills, landfills, and storage tanks have led to a more severe groundwater problem. The situations covered here used reactivated grade carbon because the treated groundwater would be used not for drinking water but for discharge to a surface water body, recharge to the aquifer, or plant process operations.

Because of the higher concentrations and, in most cases, the presence of two or more predominant contaminants, the process of choice becomes the staged system, which ensures more complete utilization of the activated carbon while maintaining the effluent at the desired level. The multistages system also allows for longer contact times required to meet the low effluent concentrations.

In some cases, pretreatment to the carbon system is necessary. Filtration may be required if the water is high in suspended solids material or dissolved iron. As we discussed in the air-stripper section, dissolved iron in the groundwater can precipitate in the activated carbon also. The carbon bed should not be used as a filter. The carbon is designed as a column operation in the first place to get the maximum use of the carbon. If the bed is backwashed to remove suspended solids, then the carbon will be mixed and the transfer zone destroyed. If the transfer zone is lost, then the carbon will only perform as it did with the

TABLE 2-9 **Carbon Adsorption with ppb Influent Levels**[a]

System No.	Contaminants	Typical Influent Conc. (μg/liter)	Typical Effluent Conc. (μg/liter)	Surface Loading (gpm/ft^2)	Total Contact Time (min)	Carbon Usage Rate (lb/1000 gal)	Operating Mode
1	1,1,1-Trichloroethane	143	< 1	4.5	15	0.4	Single fixed bed
	Trichloroethylene	8.4	< 1				
	Tetrachloothylene	26	< 1				
2	Methyl T-butyl ether	30	< 5	5.7	12	0.62	Two single fixed beds
	Di-isopropyl ether	35	< 1				
3	Chloroform	400	< 100	2.5	26	1.19	Four single fixed beds
	Trichloroethylene	10	< 1				
4	Trichloroethylene	35	< 1	3.3	21	0.21	Three single fixed beds
	Tetrachloroethylene	170	< 1				
5	1,1,1-Trichlorethane	70	< 1	4.5	30	0.45	Two fixed beds in series
	1,1-Dichloroethylene	10	< 1				
6	Trichlorethylene	25	< 1	2.0	35	0.32	Single fixed bed
	Cis-1,2-dichloroethylene	15	< 1				
7	Trichlorethylene	50	< 1	1.6	42	0.38	Two single fixed beds
8	Cis-1,2-dichloroethylene	5	< 1	1.91	70	0.25	Two fixed beds in series
	Trichloroethylene	5	< 1				
	Tetrachloroethylene	10	< 1				

[a] From O'Brien, R. and Ficher, J. L. "There is an answer to groundwater contamination." *Water/Engineering & Management*, May 1983.

TABLE 2-10 Carbon Adsorption with ppm Influent Levels[a]

System No.	Contaminants	Typical Influent Conc. (mg/liter)	Typical Effluent Conc. (mg/liter)	Surface Loading (gpm/ft^2)	Total Contact Time (min)	Carbon Usage Rate (lb/1000 gal)	Operating Mode
1	Phenol	63	< 1	1.0	201	5.8	Three fixed beds in series
	Orthochlorophenol	100	< 1				
2	Chloroform	3.4	< 1	0.5	262	11.6	Two fixed beds in series
	Carbon tetrachloride	135	< 1				
	Tetrachloroethylene	3	< 1				
	Tetrachloroethylene	70	< 1				
3	Chloroform	0.8	< 1	2.3	58	2.8	Two fixed beds in series
	Carbon tetrachloride	10.0	< 1				
	Tetrachloroethylene	15.0	< 1				
4	Benzene	0.4	< 1	1.21	112	1.9	Two fixed beds in series
	Tetrachloroethylene	4.5	< 1				
5	Chloroform	1.4	< 1	1.6	41	1.15	Two fixed beds in series
	Carbon tetrachloride	1.0	< 1				
6	Trichloroethylene	3.8	< 1	2.4	36	1.54	Two fixed beds in series
	Xylene	0.2–0.5	< 1				
	Isopropyl alcohol	0.2	< 10				
	Acetone	0.1	< 10				
7	Di-isopropyl methyl phosphonate	1.25	< 50	2.2	30	0.7	Single fixed bed
	Dichloropentadiene	0.45	< 10				

[a] From O'Brien, Robert, and Ficher, J. L. "There is an answer to groundwater contamination." *Water/Engineering & Management*, May 1983.

isotherm tests. For full utilization of the carbon, the bed must maintain its integrity.

A number of pretreatment options, such as bag filters, cartridge filters, zeolite beds, and organo clay vessels, are commercially available. Bag filters are made of disposable fabric bags in metal housings. They are capable of filtering particulates down to 1 micron. Cartridge filters perform the same function using disposable cartridges. However, both varieties of filters require regular replacement and cleaning for effective operation. Zeolite beds and organo clay vessels are useful for the removal of oils and emulsions from the waste streams. If not filtered effectively, the emulsions and oils will clog the carbon vessels and decrease the age and effectiveness of the carbon beds. Adjustment of pH may also be required if the water has a high pH and contains mineral salts susceptible to precipitation in the carbon bed. These pretreatment needs would normally be determined in the evaluation procedures.

These results, showing removal of a wide range of organic contaminants to low or nondetectable levels, indicate that granular carbon adsorption is a versatile groundwater treatment process.

APPLICATION WITH OTHER TECHNOLOGIES

Carbon adsorption is a relatively expensive process. However, the inherent advantages of the technology make it particularly suited for low concentrations of nonvolatile components, high concentrations of nondegradable compounds, and short-term projects. When there is a variety of compounds, or when very low effluent levels are required, carbon adsorption can be combined with other treatment techniques for the effective implementation of a groundwater remediation program.

Carbon adsorption may be readily combined with biological treatment to affect better overall performance. Powdered activated carbon may be added directly to the biological system to provide sites for organic compounds to adsorb and undergo biological degradation or to remove refractory organic compounds that may be toxic to the system. For possible toxic compounds, an evaluation procedure is conducted, considering specific organic compounds only. Finally, granular carbon systems can be used to polish the effluent from biological systems to remove refractory compounds.

Carbon adsorption also serves as a complementary technology to air stripping. GAC systems can be used to treat air-stripping effluent water to remove remaining volatile and nonvolatile components. Nonvolatile components such as phenols, pesticides, and other substituted aromatics can be removed in a carbon adsorption step. As air stripping is an equilibrium process, there will be some VOC concentrations remaining following the treatment step, so carbon can be used to remove those contaminants to nondetectable levels. Using air stripping as a pretreatment to carbon adsorption increases the life of the carbon. Since the more volatile contaminants tend to be those less readily adsorbed, their removal allows for the use of less carbon. In many cases, the application of both air stripping and GAC will be the most cost-effective solution.

Although this section has discussed treatment of contaminated waters, the application of GAC to treat gas streams is of importance as a complementary technology. As discussed in the air stripping section of this chapter, using air stripping may, in some cases, result in an unacceptable emission of organic compounds to the atmosphere. GAC has been proven to be effective in removing organic vapors from these exhaust airstreams.

GACs and systems for vapor adsorption are different from those normally used for liquid-phase systems. The carbon particles are usually larger to minimize the pressure drop of the gas stream, and as contaminants are easily volatilized, the systems can be designed for in situ regeneration. The pore distribution of vapor-phase carbon favors adsorption pores; therefore, equilibrium capacities for organic contaminants will be higher for vapor-phase adsorption. The evaluation of activated carbon for vapor-phase adsorption is similar, and isotherms for a variety of contaminants have been established. Pretreatment with condensers or dehumidifiers will also enhance the vapor-phase adsorption step by reducing water-vapor content and reducing the volume of the gas to be treated.

Chemical Oxidation

The use of chemical oxidation processes in the destruction or detoxification of the contaminants found in groundwater has been practiced for hundreds of years and offers distinct advantages over other technologies. Recent improvements in chemical oxidation methods are increasing application of this technology to the treatment of groundwater.

Oxidation processes involve the exchange of electrons between chemical species and effect a change in the oxidation (valence) state of the species involved. Specifically, oxidation processes are referred to as redox reactions because one of the species involved gains electrons (reduced valence state, *reduction*) and another loses electrons (increased valence state, *oxidation*). This exchange of electrons will destroy organic compounds by breaking carbon bonds and creating new, smaller compounds.

Three chemical oxidants have been traditionally used in industrial and groundwater treatment processes: chlorine, ozone, and hydrogen peroxide. In addition, oxygen has been used for some simple oxidation situations, i.e., iron removal. Permanganate compounds (sodium and potassium) and sodium persulfate have been used extensively in the remediation of contaminated soil and groundwater sites.

The use of chemical oxidants in the treatment of industrial wastewaters includes the oxidation of organic and inorganic compounds. Principal industrial uses for chemical oxidants include metals precipitation (iron, chromium), liquid and gas treatment (destruction of cyanides, sulfides), and disinfection.

The principal use of chemical oxidation in the treatment of groundwater is the ability of oxidizing agents to degrade carbonaceous compounds, theoretically to carbon dioxide and water. Adequate oxidant must be present to facilitate a complete reaction.

Principles of Oxidation

Let us first review the basic redox reaction. A redox reaction may be separated into the oxidation and reduction half-reactions, as presented here in the oxidation of ferrous iron using hydrogen peroxide (under acidic conditions):

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \tag{2-6}$$

$$2(Fe^{2+} + 3H_2O \longrightarrow Fe(OH)_3 + e^- + 3H^+) \tag{2-7}$$

In this example, the addition of hydrogen peroxide (H_2O_2) to a solution that contains ferrous iron molecules causes an electron to be stripped from the iron atom. The peroxide molecule then combines with hydrogen atoms and assumes a more stable (lower-energy) form as two water molecules.

The relative strength of an oxidant is commonly described by its electrode potential, E^o. Table 2-11 presents a summary of the standard electrode potentials for the oxidants generally used in the treatment of groundwater. The values of E^o for the oxidation and reduction half-cell elements of a redox reaction may be summed to calculate the thermodynamic potential of the reaction. This defines the level of energy input required or released during a reaction. The use of thermodynamic relations for inorganic and some simple organic oxidations corresponds

TABLE 2-11 Standard Electrode Potentials for Chemical Oxidants Used in Groundwater

Oxidant	Reduction Half-reaction	E, °V
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
Hypochlorous acid	$HOCL + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
Hypochlorite	$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90
Ozone, acidic	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Ozone, basic	$O_3 + H_2O \rightarrow O_2 + 2OH^-$	1.24
Hydrogen peroxide		
Acidic	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
Basic	$HO_{2-} + 2e^- + H_2O \rightarrow 3HO^-$	0.85
Chlorine dioxide	$ClO_2 + 2H_2O + 5e^- \rightarrow Cl^- + 4OH^-$	1.71
Oxygen		
Acidic	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
Basic	$O_2 + 2H_2O^+ + 4e^- \rightarrow 4HO$	0.40

acceptably to theory, while complex organic redox reactions tend to be driven by chemical kinetics.

If a particular redox reaction occurs readily under the standard temperature and chemical setting of the groundwater, then the addition of the oxidant to the oxidate is all that is required. However, many redox reactions require the input of energy in the form of heat, UV light, or chemical additions (such as pH alteration) or the presence of catalysts to economically facilitate a desired reaction.

Chemical Oxidants

As discussed previously, the use of oxygen, chlorine, ozone, hydrogen peroxide, permanganate, and persulfate as chemical oxidants comprise the vast majority of oxidants used in potable water, industrial water, and wastewater treatment applications. Some oxidants are reviewed below.

Oxygen

Oxygen was the first oxidant used by man and is the predominate oxidant used in nature for the destruction of wastes. In groundwater treatment, air (containing 21 percent oxygen) is principally used for the oxidation of ferrous iron to form insoluble ferric hydroxide. Atmospheric oxygen is also used in biological and other methods employed for groundwater treatment. The main cost of oxygen is the power for transferring the oxygen from the atmosphere to the water.

Chlorine

Chlorine, a powerful and widely used oxidant in water and wastewater treatment industries, has seen limited application in the treatment of groundwater. This is the result of the generation of chlorinated products and by-products. The proliferation of chlorinated species often renders the groundwater unsuitable for required purposes.

Chlorine is the most common oxidant used in water treatment. Chlorine is available in gaseous form in pressurized metal containers and is also available as a concentrated aqueous solution (sodium hypochlorite) or as a solid (calcium hypochlorite). When added to water, the reaction chemistry of the various forms is essentially the same. The primary use for chlorination is to kill bacteria in potable water supplies. Chlorine maintains a lasting residual concentration in closed water systems, which provides extended disinfection ability. The main costs of chlorine are chemical, transportation, and storage.

Ozone

Ozone is the strongest of the oxidizing agents presented in Table 2-11. Ozone occurs naturally in the earth's atmosphere by the reaction of oxygen with energy input in the form of UV radiation from the sun and during thunderstorms with energy input from lightning. Ozone is generated at the point of use with an apparatus that applies electric current to generate an electromagnetic field. The plasma or *corona discharge* excites oxygen molecules to the highly unstable ozone form. The specific yield of ozone generated by these devices is dependent on the applied voltage, frequency, design of the ozonator, and the type of feed gas used.

Ozone has properties that reduce its effectiveness as an oxidant for groundwater treatment. Ozone is so reactive that it will dissipate rapidly after contact with water, either by reacting with the constituents in the water or by spontaneous decomposition. Ozone decomposition is a complex chain-radical process that occurs based on contact with organic and inorganic molecules, stripping electrons to permit the ozone to assume more stable forms such as elemental oxygen, hydroxide molecules, and water. One ozone decomposition intermediate is the hydroxyl radical, one of the most powerful oxidizing agents known. The hydroxyl radical is capable of oxidizing almost any organic compound.

The capital and operating costs associated with the use of ozone as a chemical oxidant often limit the use of ozonation technologies. The small quantities of impurities customarily present in groundwater frequently require high levels of ozone addition for treatment, most of which decomposes spontaneously. The main cost of ozone is the capital and operating cost of the ozone generator.

Hydrogen Peroxide

Hydrogen peroxide is a stable and readily available substance and can effectively oxidize many compounds. Hydrogen peroxide is available in various commercial purities, ranging generally from 30 to 70 percent purity and in water-based solutions. Because of the relative stability of the material, it can be stored in metal, glass, and some types of plastic containers.

Hydrogen peroxide is used commercially as an oxidant for numerous organic and inorganic materials in both an aqueous and vapor form. Hydrogen peroxide is not flammable, although its strength as an oxidizer encourages the combustion of flammable materials. Care is required in preventing contact or contamination of hydrogen peroxide with organic substances. Reactive decomposition is accelerated with exposure to high temperature or UV radiation.

The rates of redox reactions involving hydrogen peroxide are often increased with the use of catalysts. Sometimes reaction products or by-products serve as catalysts, and these compounds are referred to as autocatalysts. Iron can serve as the catalyst for many hydrogen peroxide reactions, but catalyst additions should always be evaluated for this method. The reaction of iron-catalyzed peroxide oxidation at pH 2.5 to 3.5 was first discovered by H.J.H. Fenton and is known as *Fenton's reaction*. The iron/peroxide mixture is known as *Fenton's reagent*. The capital and operating costs associated with the use of hydrogen peroxide limit its application in groundwater treatment, although an increase in efficiency and effectiveness of hydrogen peroxide as an oxidant is observed when UV light is introduced.

Permanganate

In situ oxidation using permanganate is a fast-emerging technology in the remediation of contaminated soil and groundwater. There are two common forms of permanganate—potassium permanganate and sodium permanganate. Potassium permanganate is available in the crystalline form and is readily soluble in water (up to 4 percent). Sodium permanganate is available in a liquid form as a concentrated solution (40 percent) and is usually diluted in the field before application. Both forms of permanganate are strong oxidizing agents with an affinity for oxidizing organic carbon double bonds, aldehyde groups, or hydroxyl groups.

As with all oxidants, injection volumes should take into account the oxidant demand exerted by target contaminants as well as nontarget compounds. Following the injection of permanganate solutions, manganese dioxide precipitates may be formed in the subsurface, leading to decreased permeability. Potassium permanganate crystals may contain minute quantities of impurities such as barium, sodium, and chromium, which may be introduced into the subsurface through injections. This may cause a temporary exceedance in primary and secondary water quality standards in the zone of discharge. Therefore, variances (for temporary exceedance) should be obtained from the relevant regulatory authorities prior to injections.

Persulfate

Persulfate salts dissociate in water to persulfate anions, which are strong oxidizing agents. Sodium persulfate, the most common salt used in oxidation applications, is a stable, highly soluble, crystalline material that upon activation generates the sulfate radical. It is soluble in water (40 percent), and its reaction does not yield any undesirable by-products.

Sodium persulfate is "activated" through the addition of heat (steam) or a ferrous salt (iron(II)). Activation dramatically increases the oxidative strength of persulfate and is attributed to the production of sulfate free radicals that are highly reactive.

Oxidation Reactions

As discussed, numerous factors affect the selection and application of oxidants to groundwater treatment problems. The principal limitation on the cost effectiveness of the application is the concentration of contaminants in the groundwater and the quantity of excess oxidant needed to overcome spontaneous and unproductive decomposition in the aqueous medium. The reaction kinetics of a given redox reaction determines the degree of effectiveness available and the quantity of outside stimulation (in the form of a catalyst or energy input) needed to achieve an efficient and cost-effective solution.

Redox reaction rates that are developed based on the results of laboratory assessment are subject to numerous limitations such as variations in temperature and pH, the formation of reaction intermediates, and the presence and effectiveness of catalysts. Of particular concern in the recent application of chemical oxidation to groundwater treatment is the effect of temperature on reaction rates and the long-term effectiveness of the catalysts or energy sources used to stimulate reactions.

Groundwater temperature and the degree of temperature fluctuation characteristic of the source exhibit a large influence on the effectiveness of a redox process. As a rule of thumb, chemical reaction rates double with a 10°F increase in temperature. If a groundwater changes temperature on a seasonal basis, or experiences changes in temperature associated with aquifer depletion or groundwater "age," effectiveness could increase or decrease. Besides the temperature of the groundwater, the energy demands exerted by the introduction of the oxidant to the groundwater and also the effectiveness of oxidant mixing must be considered.

The effects of pH on reaction rate and effectiveness include changes in the redox reactions and quantity of available oxidant resulting from a given addition rate. Most chemical oxidants have different reaction mechanisms based on the pH range of the groundwater being treated (i.e., acidic or alkaline conditions). Some resulting reaction rates based on pH are shown on Table 2-11. The selection of a chemical oxidation technology must consider the groundwater pH and also changes in geochemistry anticipated during the life cycle of the remediation.

Advanced Oxidation Processes

Photolysis

Remediation solutions using the photolysis technologies to remediate groundwater contamination are becoming increasingly viable. The technology uses a high-energy photon (usually UV light) to cleave a peroxide molecule to generate a high-energy hydroxyl (OH^-) radical.

$$\mathrm{UV} + H_2O_2\ 2OH^-$$

The hydroxyl radical reacts with and oxidizes the organics in the groundwater. Hydrogen peroxide and ozone have been effectively utilized in applications using the concepts of photolysis.

This is a technology that should prove to destroy many organic compounds in a short amount of time and at a reasonable cost. The United States Environmental Protection Agency's (U.S.EPA's) Superfund Innovative Technology Evaluation (SITE) program has evaluated this technique and has published positive results. Several companies have set forth on major marketing campaigns to promote UV/oxidation to regulators, industries, and consultants in the groundwater field. The result has been that several UV/oxidation projects have been installed for the treatment of groundwater.

There are two basic forms in which UV/oxidation has historically been applied: UV/ozone and UV/peroxide. Figure 2-27 shows a typical setup for a UV/ozone system. Figure 2-28 shows a typical setup for a UV/peroxide system. Both systems use an oxygen-based oxidant,

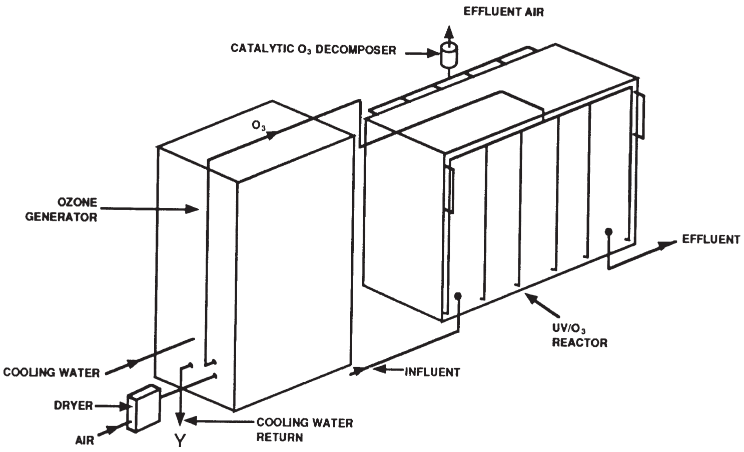

FIGURE 2-27. UV/ozone process flow diagram.

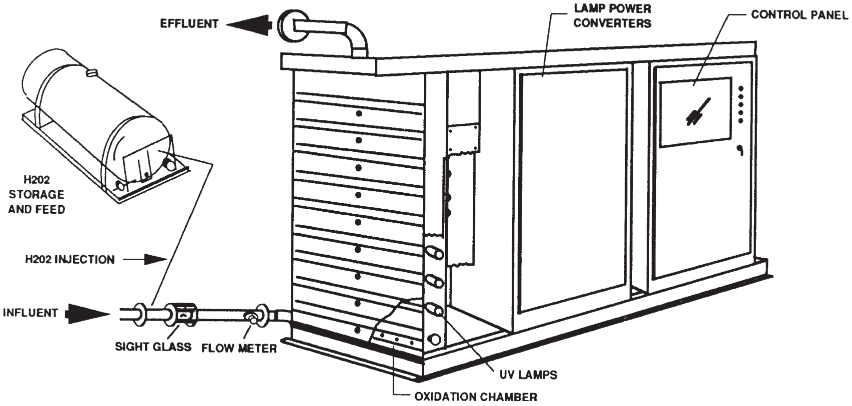

FIGURE 2-28. UV/H_2O_2 process flow diagram.

ozone for the first and hydrogen peroxide for the second. UV light is used in conjunction with the oxidant. The UV light bulbs are placed in the reactor where the oxidant comes into contact with the contaminants in the groundwater.

While ozone and hydrogen peroxide are both strong oxidizing agents, their effectiveness increases dramatically when stimulated by UV light. Figure 2-29 is an example of the difference between oxidation with the ozone alone and ozone stimulated with UV light. Similar types of increases are seen with UV and hydrogen peroxide. In both cases, the key to fast reaction times is the UV light source. However,

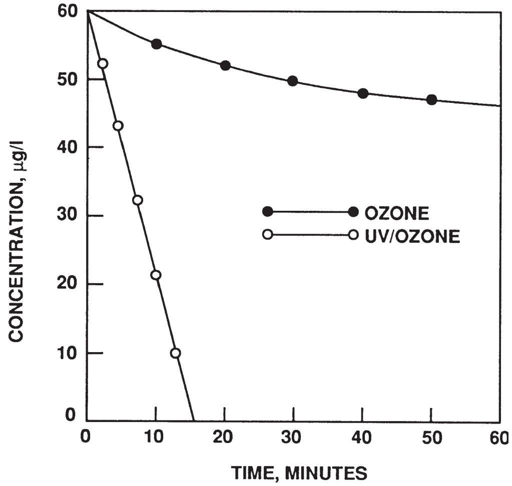

FIGURE 2-29. Oxidation of lindane with ozone and UV/ozone.

the source cannot come into direct contact with the water. The bulbs are normally covered by a quartz tube. The quartz protects the bulbs but allows the UV light to enter the water unaffected.

The main difference between the two designs is the type of oxidant and the method of application. Ozone is an unstable gas. It must be added to the reactor as small bubbles and must be produced at the site. The UV/ozone system includes an ozone generator. The ozone is sparged into the reaction tank below the UV lights. This creates a gas stream that must be evaluated for ozone and VOCs. The design in Figure 2-27 and the unit that was studied under the SITE program use *low*-intensity UV bulbs.

By comparison, hydrogen peroxide is a relatively stable liquid that can be delivered and stored on-site. The hydrogen peroxide is metered into the influent, and the main reaction occurs within the reaction tank where the UV light is present. The design in Figure 2-28 uses *high*-intensity UV bulbs. The reaction tank can be pressurized because ozone gas has no gas transfer requirements.

While these two technologies provide effective treatment of organic hazardous waste, there are potential problems with full-scale applications. The problems seem to be centered on the quartz tubes. Many chemicals and minerals in the groundwater coat out on the quartz tubes and prevent the UV light from getting into the water. This should not be unexpected with groundwater cleanups. Shallow aquifers are not normally used as sources of drinking water because they commonly contain high concentrations of dissolved minerals and other dissolved and suspended solids. Most groundwater contamination is found in shallow aquifers. There will be many natural chemicals in the water along with the contaminant that will interfere with any groundwater treatment process.

Titanium Dioxide Photocatalysis

Photocatalysis technology uses UV light to activate a titanium dioxide catalyst. The UV light generates electrons in the conduction band of the catalyst. This activates the catalyst and creates four paths of destruction for the organics: (1) by reducing oxygen and creating a superoxide radical, (2) by oxidizing a water molecule to create a hydroxyl radical, (3) by oxidation of the organic contaminant by the "activated" titanium dioxide, and (4) reduction of the contaminants by the conduction band electron. The application can be designed to use the titanium dioxide catalyst in the slurry form or fixed form.

In the former case, the influent groundwater after filtration is mixed with titanium dioxide (catalyst) slurry and passed over protected UV light bulbs. The UV light activates the catalyst, and oxidation of organic target compounds is accomplished. The catalyst is filtered from the effluent stream and recovered for reuse. In the fixed-bed catalyst design, influent is passed through a catalyst bed and exposed to UV light. The fixed-bed design has been found to be difficult to maintain and operate and is undergoing design changes.

The biggest difference between titanium dioxide photocatalysis and UV/peroxide oxidation technologies is the way the radicals are generated. The titanium dioxide photocatalytic method relies on activating a catalyst and is more energy efficient because it requires photons of wavelengths of less than 388 nm to excite the catalyst, unlike the UV/peroxide oxidation technology that has to cleave the peroxide molecule to generate the hydroxyl radical. The photocatalysis process does not depend on the transmittal of UV light through the water column and therefore is not affected by water quality issues such as total dissolved solids, turbidity, or color.

Miscellaneous Treatment Methods

New technologies are constantly being introduced to the groundwater market. Most of these technologies were previously used in industrial processes. Some are completely new to the area. As these systems are applied in the field, more will be published about each technology. The reader's knowledge base will have to be continually updated.

In general, a shift in technological development has been evident in the last several years. Treatment systems are moving away from a phase-change approach to destructive treatment. Constituent removal and total destruction are more desirable in that they not only remediate the process stream but also eliminate the liability associated with phase-change technologies. Some of the more interesting and significant new treatment methods are discussed in the following sections.

Thermal Oxidation

Incineration is the raising of both water and contaminants to high temperatures in the presence of oxygen, resulting in carbon dioxide, water, and other products of combustion. One application of thermal oxidation is in the use of flame incinerators, where either a sufficient quantity of VOCs or supplemental fuel is used to maintain a flame burning in the 1,500 to 2,000°F range. When waters contain approximately 20 percent organics, the contaminated water will have a self-sustaining burn. At concentrations below this level, auxiliary fuel is required. At lower concentrations, this can become very expensive. Between adsorption in the unsaturated zone and dilution by the groundwater, concentrations are rarely this high in groundwater. These incinerators, while effective and in current use, require an intensive trial burn and permitting process. Another problem is the high capital cost of incinerators. Finally, groundwater remediation usually contains too small a volume of highly contaminated water. If the groundwater site is close enough to an existing incinerator, then the application for small volumes of highly toxic materials may be possible.

A development in incineration technology is the nonflame, packed-bed thermal incinerator. Field applications to date have included chlorinated hydrocarbons to a destruction efficiency of 99.99 percent. The corrosion-resistant, continuous-feed unit is packed with ceramic beads that are preheated to temperatures between 1,900 and 2,000°F. Contaminated gases, in the presence of oxygen, are forced through the heated ceramic beads and are mixed by turbulence, whereby complete combustion is achieved. Levels of nitrous oxides are reduced and the formation of furans and dioxins is minimized by the uniform heating conditions below 3,000°F. Additionally, safety devices required in open-flame units are not needed. A broad range of airflows may be accommodated with these units from 1 to $>$1,000 cfm.

Although expensive, capital costs for nonflame, packed-bed incinerators are comparable to on-site regenerative carbon systems. When compared to off-site carbon regeneration, costs are attractive. Care must be taken in evaluating applicability as final costs will be influenced by fuel needs and influent stream complexities. Nonflame incinerators have not been successful in treating fluorinated compounds.[2] Once again, groundwater is usually too "clean" to make use of this technology.

Probably the most widely applied thermal method is catalyzed thermal oxidation, using either metals or inorganic acids as the catalyst. These units are applied to air treatment from vapor extraction systems or off-gas treatment from air strippers. Metal-catalyzed oxidation is designed for destruction efficiencies from 90 to 98 percent and is a function of the temperature of the catalyst bed, quantity of catalyst, and type of metal used.[2] The contaminated airstream is preheated by reusing waste heat and a burner, if required. Preheated air passes through the metal catalyst, which, in the presence of oxygen, promotes combustion reactions with temperatures ranging between 500 and 1,000°F. The catalyst surface lowers the activation energy required to cause the oxygen to react with the contaminant hydrocarbons.[22] Products of combustion, water and carbon dioxide, are emitted by stack discharge after passing through a heat exchanger as indicated earlier.

The difference between metal catalysts lies in the component material and physical structure. Base metals such as copper, manganese, and cobalt are used as are precious metals including platinum, palladium, and rhodium. Selection of less expensive base metals would be appropriate for fluidized bed reactors that require periodic replenishment of the metal catalyst. Although expensive, precious metal catalysts have been found effective at lowering operating temperatures and additionally are resistant to contaminants.

The physical forms of metal catalysts that have been successfully used are pelleted and honeycomb forms. Pelleted forms, used in fluidized beds, must operate within a narrow contaminant gas flow rate to eliminate channeling and bed collapse and, therefore, require carefully controlled, operator-assisted start-up. Although the catalyst is not consumed in the combustion reaction, breakdown of the pellets occurs in a fluidized bed as a result of friction. The last catalyst has to be continually replaced.

Catalyst performance is influenced by a number of conditions: thermal aging, poisoning, and masking of the catalyst. Thermal aging reduces the catalyst activity by sintering of the surface area of base metals. In precious metals, sintering of the surface area occurs as a result of crystallite migration. Sintering occurs with temperatures in excess of 1,400°F, an unusual condition in catalytic thermal oxidation.

Catalyst poisoning occurs when contaminants in the waste stream react with catalyst metal sites, thus reducing catalytic activity. Potential poisons include halogens and phosphorous. For precious metals, poisoning is an adsorptive phenomenon that may be reversed by desorption, while base metals poisoning is irreversible because it is not possible to clean with chemical solutions that solubilize the base metals.

Masking of the metals catalyst is the covering or “masking” of available catalytic sites, which reduces catalyst activity. This condition occurs when the process is operated at too low a temperature, resulting in char formation. Masking compounds may be removed with either acid or base solutions or a combination of both.

Low-temperature catalytic oxidation is selected when influent stream organic concentrations are low, requiring supplemental fuel for flame thermal incineration. A benefit also to be considered in catalytic thermal oxidation is lowered nitrous oxide and carbon dioxide emissions associated with lower fuel consumption.

Chemical Oxidation

The previous section was devoted to oxidation methods. One further new oxidation method, liquid-phase oxidation using an inorganic acid catalyst is an emerging technology. In this method, the contaminated liquid stream is mixed with an inorganic acid solution such as phosphoric acid, an oxidant, and heated to temperatures in the range of 250 to 500°F. The acid-catalyzed oxidation reaction results in the dissolution of contaminants, the oxidant, and the catalyst in the liquid phase. The by-products of this reaction mechanism are nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen, and water; with the ratio of carbon monoxide to carbon dioxide in the 33-percent range. The addition of a transition metal in small quantities has shown to improve catalytic action and achieve destruction efficiencies $>$ 99 percent. This technology has been proven effective in the reduction of pesticides and a herbicide.[23]

Membrane Technology

Two types of membrane technology are noteworthy: diffusion membrane separation and pervaporation membrane separation. Diffusion membrane separation involves a nonporous membrane, which, unlike reverse osmosis membrane, is permeability selective. The system operates with a low pressure gradient, approximately 35 psi, which causes diffusion of water through the membrane. Impermeability of hydrocarbons causes these compounds to be retained by the membrane. The structure and orientation of the membrane polymer chains affect the degree of permeability afforded the membrane. Pilot studies have shown the effectiveness on halogenated and nonhalogenated compounds, with less fouling than in standard "filtration" systems. Other advantages to this technology are the low operating pressure and effectiveness in treating oily substances.

Like diffusion membrane separation, pervaporation membrane separation is a perm-selective technology. Liquid feed-containing contaminants contact the membrane on one side and are removed as a vapor on the other. The phase change in commercial operations is accomplished by maintaining a vapor pressure on the permeate side that is less than the vapor pressure on the liquid feed side. The vapor pressure is created by maintaining a low pressure on the permeate side by spontaneous condensation of permeate vapor. Control of the liquid condensate conditions determines the vapor pressure. Solvent removal of benzene in bench-scale experiments indicates a 99-percent efficiency. The effluents of this system are a purified groundwater, as well as a condensed, concentrated permeate liquid. The necessity of disposal and the associated liability of this phase transport technology is one of the main disadvantages of the technology.[24] Pervaporation is applicable to groundwater, leachate, or wastewater treatment. In comparison to carbon adsorption treatment, pervaporation does not entail competition between compounds in a multicomponent stream for active adsorption sites. Compounds absorbed on the pervaporation perm-specific membrane are continuously removed as vapor. There are advantages of pervaporation when compared to air stripping. As no air is injected into the pervaporation system, the fouling problems experienced because of oxygen saturation do not occur. Additionally, the need for expensive air-phase, off-gas treatment is not required. One final advantage is that pervaporation is not limited to those compounds with high Henry's law constants. The major technical disadvantage to pervaporation treatment is in the management of the concentrated permeate stream.[25]

Supercritical Extraction

Supercritical extraction uses a liquid or gas at or near its critical point to act as an enhanced solvent for the removal of hazardous compounds from process streams. There is also evidence that supercritical liquid extraction is effective in the removal of aromatic hydrocarbons from sandy loam soil.

Liquids or gases at or near their supercritical point have an increased solvent action while maintaining their original diffusivities and viscosities. Controlling the pressure and temperature will control the extraction and separation process by affecting the ability of a fluid to act as a solvent. The system influent, composed of a solid or liquid contaminant-containing stream, is introduced into a reactor vessel and mixed with the supercritical solvent. After the extraction of contaminants, the supercritical solvent/contaminant stream is drawn off to a separator vessel, where pressure reduction causes vaporization of the supercritical solvent and condensation of the contaminants. The contaminant stream is collected for disposal, while the solvent is repressurized to its critical state for reuse.

Liquid carbon dioxide has been shown to be effective in the extraction of nonvolatile-type compounds, such as polychlorinated biphenyls (PCBs), pesticides, and phenol, from both liquid and soil systems. Several factors and conditions increase the efficiency of extraction, such as the addition of cosolvents to increase the solubility of carbon dioxide with multiring polynuclear aromatic hydrocarbons (PAHs). Water has been shown to decrease the adsorptive ability of PAHs on soil, thereby improving its extractability under supercritical conditions. Generally, the more rings a PAH has, the greater difficulty there will be to achieve good extraction. Cosolvent addition has been shown to increase efficiency with multiring PAHs by 20 to 30 percent. Although supercritical extraction occurs at high pressures in the range of 900 to 1,200 psi, moderate to ambient temperatures are possible for many applications.[26]

Emerging Technologies

A number of processes are now briefly mentioned to complete this discussion of technologies.

E-beam Technology

An attractive treatment for low-concentration (μg/L) organics, such as chloroform, trichloroethene, tetrachloroethene, substituted benzene, and trihalomethanes, is high-speed electron beam (E-beam) technology. E-beam technology has shown removal efficiencies up to 99.99 percent in full-scale operation. An electron beam passing through a thin sheet of water initiates chemical reactions to reduce contaminants to carbon dioxide, water, and salt. Currently, this process has been accepted into the SITE program.[27]

Micellar-enhanced Ultrafiltration

Micellar-enhanced ultrafiltration differs from conventional ultrafiltration by the addition of a surfactant to the waste stream. Contaminants are collected by the surfactant-based micelles, which are created through ionic attraction and, based on solubility, are incorporated in the macromolecular structure. The ability to treat organics and/or heavy metals is influenced by the type of surfactant selected with respect to its ionic charge. Anionic, negatively charged surfactants have the capability to absorb heavy metals, while positively charged cations are effective in organic removal but cannot remove metals. Removal efficiencies are reported at >99 percent for divalent zinc, divalent copper, hexane, chlorophenol, and 4-*tert*-butylphenol and >97 percent for cresol. Solubilized contaminants and their micelles are collected in a concentrate stream for disposal, with the resulting clean filtrate available for use as desired. Some leakage in ultrafiltration of pure surfactant has been observed, but it is nontoxic, and literature reports the concentration of the biodegradable substances to be less than 100 ppm.[28]

Zero-valent Iron

Another in situ technology gaining popularity is zero-valent iron (ZVI). Use of this technology typically involves the establishment of a funnel-and-gate-type system, with placement of a reactive barrier wall containing the ZVI in the gate. Effective removal of chlorinated solvents from groundwater by ZVI is well established. Treatment is achieved by reductive dehalogenation, in which a chlorine atom is replaced by a hydrogen atom. For polyhalogenated compounds, the reaction can continue until all halogens have been removed. ZVI can also be used for the reduction of nitrate and Cr(VI).

References

1. Olsen, R., and A. Davis, Predicting the fate and transport of organic compounds in groundwater, Hazardous Materials Control, May/June 1990.
2. Davis, J.B., et al., The Migration of Petroleum Products in Soil and Groundwater, American Petroleum Institute, December 1972.
3. Yaniga, P.M., Groundwater abatement techniques for removal of refined hydrocarbons, Hazardous Wastes and Environmental Emergencies Proceedings, March 1984. HMCRI.
4. Suchomel, K., et al., Production and transport of carbon dioxide in a contaminated vadose zone: A stable and radioactive carbon isotope study, Environmental Science and Technology, December 1990.
5. Payne, F.C., S. Potter, and J. Quinnan, Remediation Hydraulics, CRC Press, Boca Raton, FL, 2008.
6. Lenzo, E.C., T.J. Freilinghaus, and A.W. Zienkiewicz, The application of the Onda correlation to packed column air stripper design: Theory versus reality, AWWA National Conference Proceedings, 1990.

7. Sullivan, K., and E. Lenzo, Groundwater treatment techniques—An overview of the state-of-the-art in America, First US/USSR Conference on Hydrogeology, Moscow (NWWA), July 3–5, 1989.
8. United States Environmental Protection Agency, U.S. Federal Register, 40 Code of Federal Regulations, parts 141 and 142. National Primary Drinking Water Regulations, pp. 25690–25717, July 8, 1987.
9. Nicholson, B.C., et al., Henry's law constants for the trihalomethanes: Effects of water composition and temperature, Environmental Science and Technology, 18: 7-518, 1984.
10. Roberts, P.V., G.D. Hopkins, C. Munz, and A.H. Riojas, Evaluating two resistance models for air stripping of volatile organic contaminants in a countercurrent, packed column, Environmental Science and Technology. 19: 164–173, 1985.
11. Cummins, M.D., Economic Evaluation of TCE Removal from Contaminated Ground Water by Packed Column Air Stripping (DRAFT), 1985.
12. Cummings, M.D., Field Evaluation of Packed Column Air Stripping Miami, FL USEPA-ODW-TSD, 1988.
13. Cummings, M.D. Field Evaluation of Packed Column Air Stripping for THM Removal, Virginia Beach, VA, USEPA-ODW-TSD, 1984.
14. Staudinger, J., W.R. Knoche, and C.W. Randall, Evaluating the Onda mass transfer correlation for the design of packed column air stripping, AWWA Journal pp. 73–79, 1990.
15. Carlton, G.M., Utilizing air stripping technology for pretreatment of solvent waste. Proceedings of Solvent Waste Reduction Symposium, pp. 14–32, 1986.
16. United States Environmental Protection Agency, Air Toxics Control Technology Center, Air Strippers Air Emissions and Controls (DRAFT) DCN No. 87-231-02032-16, 1987.
17. Crittenden, J., et al., An evaluation of the technical feasibility of air stripping solvent recovery process, American Water Works Association Research Foundation, June 1987.
18. Zanden, A.K., M.J. Semmens, and R.H. Marbaitz, Removing VOCs by membrane stripping, AWWA Journal, pp. 76–81, November 1989.
19. Zanden, A.K., R. Qin, and M.J. Semmens, Membrane/oil stripping of VOCs from water in hollow fiber contactor, ASCE Journal of Environmental Engineering. 115(4), August 1989.
20. Foster, R., N. Lewis, I. Topudurti, and G. Weishans, A field demonstration of the UV/oxidation technology to treat groundwater contaminated with VOCs, Control Technology, Air & Waste Management Assoc.
21. Bernardin, F.E., Jr., UV/peroxidation destroys organics in groundwater. 83rd Annual Meeting of the Air and Waste Management Assoc, Pittsburgh, PA, June 24–29, 1990.
22. Fletcher, D.B., UV/ozone process treats toxics, Waterworld News, 3(3), May/June 1987.

23. Roy, K.A., Scientists set to destroy VOCs with thermal oxidation process, Hazmat World, December 1989.
24. Herbert, K.J., Catalysts for volatile organic compound control in the 1990s, Paper presented at the 1990 Incineration Conference, May 1990.
25. Burns, K.R., Use of catalysts for VOC control, Paper presented at the New England Environmental Expo, Boston, MA, April 1990.
26. Leavitt, D., et al., Homogeneously catalyzed oxidation for the destruction of aqueous organic wastes, Environmental Progress, Vol. 9, November 1990.
27. Roy, K.A., High speed electrons race toward water cleanup, Hazmat World, December 1990.
28. Wijmans, J.G., et al., Treatment of organic-contaminated wastewater streams by pervaporation, Environmental Progress, Vol. 9, November 1990.

29. Lipski, C., and P. Cote, The use of pervaporation for the removal of organic contaminants from water, Environmental Progress, Vol, 9, November 1990.
30. Andrews, A.T., et al., Supercritical fluid extraction of aromatic contaminants from a sandy loam soil, Environmental Progress, Vol. 9, November 1990.
31. A guide to innovative nonthermal hazardous waste treatment processes, Special Feature Article, *The Hazardous Waste Consultant*, November/December 1990.

3

Treatment of Organic Contaminants: Biological Treatment

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One of the most promising treatment technologies for groundwater is biological treatment. During the thirty years that we have worked on groundwater, we have seen biotechnology go from snake oil to an advanced technology. Our government is now strongly behind bioremediation—"If we have a magical torch, it's biotechnology research."[1]

With all of this attention, it is important to understand what biological treatment can really do because biological treatment cannot be applied to every situation. We have to understand biotechnology's abilities and limitations before we broadly apply it to groundwater situations. To correctly apply biotechnology, we have to understand the biochemical reactions of the microorganisms, and we have to understand the equipment designs used to apply those microorganisms to groundwater. There is a large difference between what a bacterium can do with specific organic compounds and what an activated sludge treatment system can do with a specific groundwater situation.

Accordingly, this chapter begins with a detailed review of microorganisms and their biochemical reactions with hazardous organic compounds. Next, we review how these reactions have been applied to groundwater cleanups.

MICROORGANISMS

Free-living microorganisms that exist on earth include bacteria, fungi, algae, protozoa, and metazoa. Viruses are also prevalent in the environment, but these particles can exist only as parasites in living cells

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of other organisms and are not discussed in this text. Microorganisms have a variety of characteristics that allow survival and distribution throughout the environment. They can be divided into two main groups: eucaryotes and procaryotes. The eucaryotic cell is the unit of structure that exists in plants, metazoa animals, fungi, algae, and protozoa. The less complex procaryotic cell includes bacteria and cyanobacteria.

Even though the protozoa and metazoa are important organisms that affect soil and water biology and chemistry, they do not perform important degradative roles. Therefore, this chapter concentrates on bacteria and fungi.

The bacteria are by far the most prevalent and diverse organisms on earth. There are over 200 genera in the bacterial kingdom.[2] These organisms lack nuclear membranes and do not contain internal compartmentalization by unit membrane systems. Bacteria range in size from approximately 0.5 micron to seldom greater than 5 microns in diameter. The cellular shape can be spherical, rod-shaped, filamentous, spiral, or helical. Reproduction is by binary fission. However, genetic material can also be exchanged between bacteria.

The fungi, which include molds, mildew, rusts, smuts, yeasts, mushrooms, and puffballs, constitute a diverse group of organisms living in freshwater and marine water but predominantly in soil or on dead plant material. Fungi are responsible for mineralizing organic carbon and decomposing woody material (cellulose and lignin). Reproduction occurs by sexual and asexual spores or by budding (yeasts).

Distribution and Occurrence of Microorganisms in the Environment

Because of their natural functions, microorganisms are found throughout the environment. Habitats that are suitable for higher plants and animals to survive will permit microorganisms to flourish. Even habitats that are adverse to higher life forms can support a diverse microorganism population. Soil, groundwater, surface water, and air can support or transport microorganisms. Soil, groundwater, and surface water environments support microorganism growth, while the air acts as a medium to distribute organisms to other environments.

For example, there are several genera of bacteria and fungi in soil and water capable of hydrocarbon degradation. The predominant bacteria genera[5, 6] include *Pseudomonas*, *Bacillus*, *Arthrobacter*, *Alcaligenes*, *Corynebacterium*, *Flavorbacterium*, *Achromobacter*, *Micrococcus*, *Nocardia*, and *Mycobacterium*. The predominant fungal genera[7] include *Trichoderma*, *Penicillium*, *Asperigillus*, *Mortierella*,

TABLE 3-1 Microorganism Population Distribution in Soil and Ground Water

Organism	Population Size	
	Typical	Extreme
	Surface soil (cells/gram soil)	
Bacteria	0.1-1 billion	>10 billion
Actinomycetes	10-100 million	100 million
Fungi	0.1-1 million	20 million
Algae	10,000-100,000	3 million
	Subsoil (cells/gram soil)	
Bacteria	1,000-10,000,000	200 million
	Ground water (cell/ml)	
Bacteria	100-200,000	1 million

and *Phanerochaete*. Table 3-1[13] shows the microorganism population distribution in soil and groundwater and demonstrates the variability and population sizes that can exist.

Soil

Bacteria outnumber the other organisms found in a typical soil. These organisms rapidly reproduce and constitute the majority of biomass in soil. Typically, microorganisms decrease with depth in the soil profile, as does organic matter. The population density does not continue to decrease to extinction with increasing depth, nor does it necessarily reach a constant declining density. Fluctuations in density commonly occur at lower horizons. In alluvial soils, populations fluctuate with textural changes; organisms are more numerous in silty or silty clay horizons than in intervening sandy or course sandy horizons. In soil profiles above a perched water table, organisms are more numerous in the zone immediately above the water table than in higher zones.[3] Most fungal species prefer the upper soil profile.

Groundwater

Microbial life occurs in aquifers. Bacteria exist in shallow to deep subsurface regions, but the origins of these organisms are unknown. They could have been deposited with sediments millions of years ago, or they may have migrated recently into the formations from surface soil. Bacteria tend not to travel long distances in fine soils but can travel long distances in course or fractured formations. These formations are susceptible to contamination by surface water and may carry pathogenic organisms into aquifer systems from sewage discharge, landfill leachate, and polluted water.[4]

In all of these ecosystems, multiple types of bacteria exist. In fact, all degradation processes require multiple microorganisms working in concert. Also, more than one type of bacteria or fungi can perform the same degradation function. When investigating microorganisms for the degradation of specific organic compounds, it is more important to demonstrate the ability to degrade a compound than to locate a specific bacteria or fungi.

Over the years that this book has been published, the above paragraph has become very controversial. Many resources have been committed to finding, separating, producing, and eventually selling specific microorganisms. For some reason, scientists get a great deal of pleasure from separating microorganisms and placing names on them. In the beginning, this was limited to aerobic environments. It is very difficult to culture single anaerobic populations in the laboratory. However, with the advent of ribonucleic acid (RNA)-detecting techniques, anaerobic bacteria have joined the great game.

To put it simply, there are two main camps. One believes that single bacteria are responsible for the success of remediations. This camp believes that everything should be done to find, enhance, and/or add these bacteria to a site. The other camp believes that multiple bacteria are responsible for all remediations, and those bacteria are ubiquitous. This camp believes that everything should be done to create the correct environment to enhance the right bacterial population. Bacteria or environment? The previous paragraph puts this book into the environment camp. The original paragraph was published over thirty years ago. With thirty more years of experience, the authors are more firmly in the environment camp than ever. That is not to say that specialized bacteria are not a good tool on some remediations. But in over thirty-five years of experience, the authors can count on one hand the number of times that specialized bacteria have been useful on remediations.

Microorganism Biochemical Reactions

Microorganisms degrade organic compounds to obtain energy that is conserved in the carbon–hydrogen (C–H) bonds of the compounds. The organics are converted to simpler organic compounds, and ultimately to carbon dioxide or methane and water. The microbes will also use part of the compounds as building blocks for new microbial cells.

Microorganisms have been used by man to degrade organic compounds for many years. Biodegradation is the process where indigenous microorganisms convert or degrade natural and man-made organic compounds. Carbon sources not produced by any natural enzymatic process or having unnatural structural features are considered xenobiotic. Compounds that are naturally occurring and exist in increased concentrations as a result of human activities are also considered xenobiotic.[9]

The main goal of a bioremediation design is the destruction of organic hazardous waste. However, we must remember that this is not the main goal of the bacteria and the fungi. The main function of bacteria and fungi is the degradation of natural organic material. This, in turn, is part of the natural carbon cycle[3] of the earth, Figure 3-1.

As can be seen in Figure 3-1, the microorganisms perform a small part of the overall carbon cycle. When we discuss hazardous waste destruction, we are referring to a small part of the natural microorganism's activity. We are simply recycling man-made carbon compounds back into the natural carbon cycle. It is helpful to keep these ideas in mind when we are designing biological systems. We are adjusting natural systems, not creating new ones. In fact, most of the time, we will find that degradation is already occurring and that the main design objective is to enhance an ongoing reaction.

Biodegradation of organic compounds (and maintenance of life-sustaining processes) are reliant upon enzymes. There are numerous enzyme systems in bacteria that perform highly specific reactions. These biological reactions hasten and regulate cellular activity such as energetics and biosynthesis. Enzymes are proteins produced by living organisms that catalyze cellular reactions. These proteins exist within cellular cytoplasm, attached to cellular membranes, and attached to

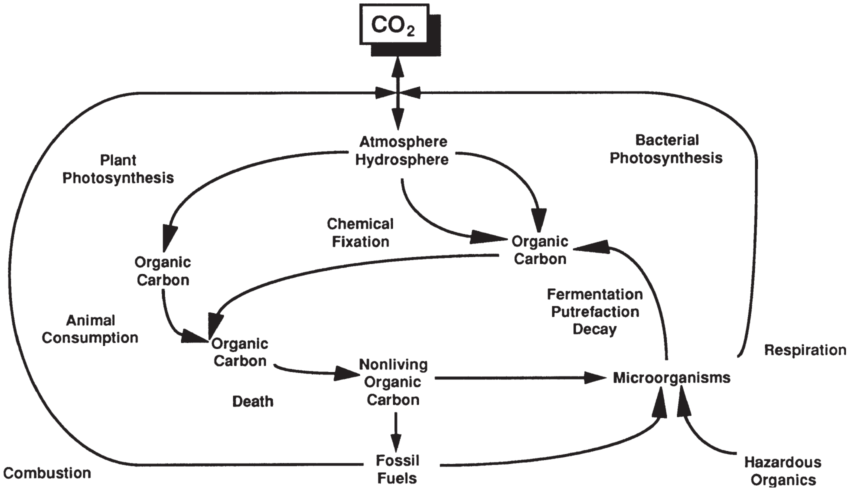


FIGURE 3-1. Carbon cycle.

the outside of the cell wall. Reactions are catalyzed when the organic substrate collides and binds to the active site of the enzyme. Substrate activation allows the enzyme to react and produce the product and restore the enzyme.[8]

The best way to understand enzyme reactions is to think of them as a lock and key. Figure 3-2 shows how only an enzyme with the right shape (and chemistry) can function as a key for the organic reactions. The key and lock in Figure 3-2 are two dimensional. In the real world, the enzyme and organic chemical are three dimensional. The fit between the two has to be precise. Thus, isomers and stereochemistry can play an important role in the effectiveness of a biological treatment method. For instance, the 2,6-dinitrotoluene isomer is recalcitrant to most bacteria capable of using the 2,4-dinitrotoluene isomer as a source of carbon. A pilot study conducted at a former munitions manufacturing facility demonstrated the need to introduce a bacterial isolate capable of degrading the 2,6-dinitrotoluene isomer to supplement the overall effectiveness of the microbial community.[36]

Organic compounds in the environment that are degradable align favorably with the active site of the specific enzyme. Persistent compounds do not align favorably, and recalcitrant compounds do not bind with the enzyme's active site. Degradation of persistent or recalcitrant compounds require that the microorganism population adapts in response to the environment by synthesizing enzymes capable of catalyzing the degradation of those compounds.

The action of enzymes is limited by two basic factors. The physical constraints of the active site within the enzyme molecule result in a

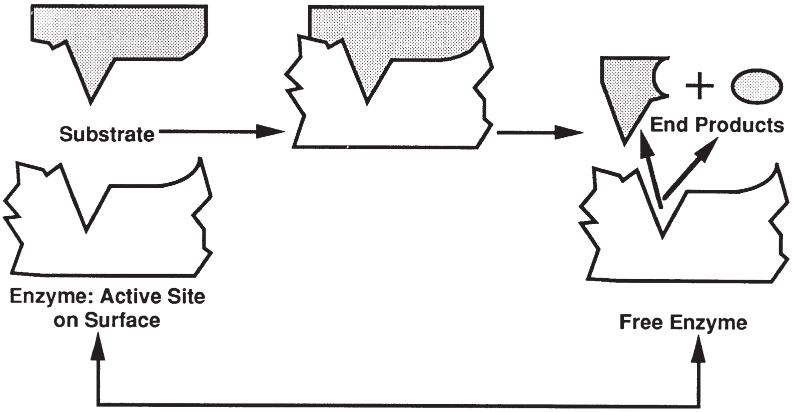


FIGURE 3-2. Enzymes are represented as a lock and key.

series of kinetic limitations referred to as enzyme inhibition. Extracellular enzymes are also susceptible to proteases (protein-cleaving enzymes) that may be present in the environment.[9]

Organisms generally derive energy from redox reactions (catabolism). Enzyme-mediated redox reactions are the transfer of electrons from electron donors to acceptors. Energy is derived from these reactions where the energy source (electron donor) is oxidized, transferring electrons to an acceptor and releasing energy conserved in the chemical bond. After the electron donor has been completely oxidized, the compound is no longer a source of energy. Bioremediation processes where microorganisms are exploited to degrade xenobiotic compounds are *identical* to natural degradative processes requiring enzymes. The energy released from these compounds is used by the organism to maintain life-sustaining processes.

Organisms conserve the energy generated during a redox reaction by transferring the energy to high-energy phosphate bonds. The most important high-energy phosphate compound in living organisms is adenosine triphosphate. Adenosine triphosphate is generated and used during biosynthesis reactions requiring energy expenditures.

Adenosine triphosphate is synthesized in a variety of mechanisms. Organic and inorganic compounds and light energy can be used to synthesize adenosine triphosphate. Organic compounds provide energy sources for all animals and most microorganisms, including all fungi, protozoa, and most bacteria. The biochemical pathways where adenosine triphosphate is generated can be divided into three major groups: (1) fermentation, in which oxidation occurs in the absence of added electron acceptors; (2) aerobic respiration, in which molecular oxygen serves as the electron acceptor; and (3) anaerobic respiration, in which a compound other than oxygen, such as nitrate, sulfate, or carbonate, serves as the electron acceptor.[8]

Biosynthetic processes in which microorganisms synthesize compounds that they require are termed *anabolism*. These are complex enzymatic processes in which simple compounds are synthesized into complex compounds. These processes require energy generated in the catabolic reactions. The combination of catabolic and anabolic processes is called *metabolism* and refers to all degradative and biosynthetic reactions within cells.

Factors That Affect Biochemical Reactions

Several factors are necessary to maintain microorganisms' metabolic processes. Optimization of these factors will provide conditions that are conducive to support biodegradation. However, optimization is affected by factors that may be limited in the environment. Any factor (carbon substrate, oxygen, inorganic nutrients) can limit the biodegradation rate of xenobiotic compounds. It is necessary therefore to establish an environment in which the limiting factor(s) are the xenobiotic compounds: this known as a substrate-limited environment. This will assure that biochemical processes will be able to effectively degrade these compounds. The main objective of most aboveground and in situ designs is to create an environment that does not limit the microorganism's rate of growth.

This process is illustrated in *Leibig's law of the minimum*, where the rate of biological processes is limited by the factor present at its minimum level. This law can also be extended to demonstrate that any growth factor can be toxic to biological processes if the concentrations are too high. Therefore, optimal conditions are those in which necessary factors are not consumed or concentrations are not too high to inhibit growth. Even oxygen or water at too high a concentration can be harmful (toxic) to the biochemistry of the cell. On the other hand, the most toxic compound known will have a minimum concentration at which it no longer affects the microorganism. Figure 3-3 illustrates Leibig's law.

Electron Acceptor

As mentioned above, there are three mechanisms used by microorganisms to produce energy. Fermentative processes rely on organic

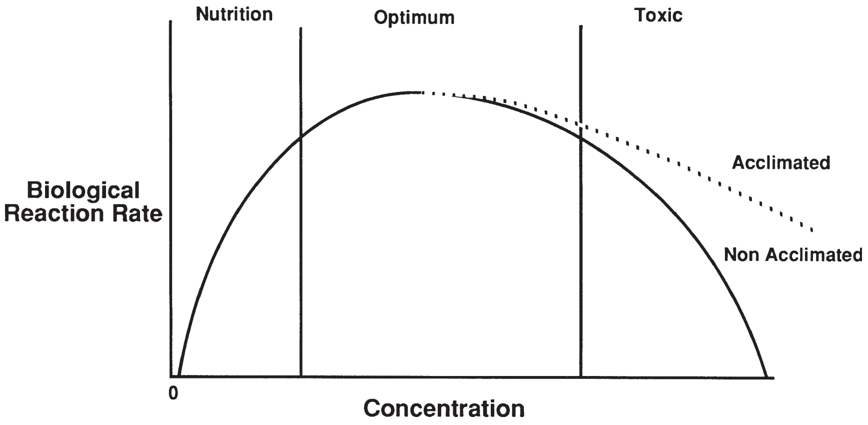


FIGURE 3-3. Leibig's law.

compounds as electron donors and acceptors; respiration processes require oxygen; and anaerobic processes rely on nitrate, sulfate, or carbonate in the absence of oxygen to complete organic compound oxidation. Microorganisms that require molecular oxygen are termed obligately aerobic. These organisms cannot survive without oxygen. Within this group, there are microorganisms that survive on reduced oxygen concentrations and are termed microaerophilic. Microaerophilic organisms' enzyme systems are actually inactivated under strong oxidizing conditions (partial pressure greater than 0.2 atm).[10] Microorganisms that do not obtain energy using molecular oxygen and are inhibited or killed by molecular oxygen are termed obligately anaerobic. Microorganisms that can survive and grow either in the presence or absence of molecular oxygen are termed facultative anaerobes. In metabolic terms, facultative anaerobes comprised two subgroups. Some (lactic acid bacteria) have an exclusively fermentative energy-yielding metabolism but are not sensitive to the presence of oxygen. Others can shift from aerobic to anaerobic with the absence of molecular oxygen and in the presence of nitrate or sulfate.[10]

Generally, an oxygen atmosphere in soil of less than 1 percent will change metabolism from aerobic to anaerobic.[3] In aqueous environments, an oxygen concentration less than approximately 1.0 mg/L can switch metabolism from aerobic to anaerobic.[11] Microaerophobic bacteria maintain aerobic reactions at reduced oxygen levels.

Inorganic Nutrients

Molecular composition of cells is fairly constant and indicates the requirements for growth. Water constitutes 80 to 90 percent of cellular weight and is always a major nutrient. The solid portion of the cell is composed of carbon, oxygen, nitrogen, hydrogen, phosphorus, sulfur, and micronutrients. The approximate elementary composition is shown in Table 3-2.[10]

As can be seen in Table 3-2, the largest component of the bacteria is carbon. The organics that we wish to destroy will provide this element. After carbon, oxygen is the highest percentage of the cell. When this is added to the oxygen required as the electron acceptor, large amounts of oxygen are utilized in biological degradation. In fact, oxygen is usually the limiting factor in biochemical reactions. Most of the operating costs of a biological treatment system come from the supply of oxygen to the bacteria.

The other major nutrients required by the microorganisms are nitrogen and phosphorous. This can also be seen in Table 3-2. The three

TABLE 3-2 Molecular Composition of a Bacterial Cell

Element	Percentage of Dry Weight
Carbon	50
Oxygen	20
Nitrogen	14
Hydrogen	8
Phosphorus	3
Sulfur	1
Potassium	1
Sodium	1
Calcium	0.5
Magnesium	0.5
Chlorine	0.5
Iron	0.2
Others	~0.3

forms of nitrogen found in microorganisms are proteins, microbial cell wall components, and nucleic acids. The most common sources of inorganic nitrogen are ammonia and nitrate. Ammonia can be directly assimilated into amino acid synthesis. When nitrate is used, it is first reduced to ammonia and then synthesized into organic nitrogen forms.

Phosphorus in the form of inorganic phosphates is used by microorganisms to synthesize phospholipids and nucleic acids. Phosphorous is also essential for the energy transfer reactions of adenosine triphosphate. Organic phosphate compounds occur in nature and are also used by microorganisms. Phosphatase enzymes that hydrolyze the organic phosphate ester are present in nearly all organisms.[8]

Micronutrients are also required for microbial growth. Several micronutrients are universally required, such as sulfur, potassium, magnesium, calcium, and sodium. Sulfur is used to synthesize two amino acids, cysteine and methionine. Inorganic sulfate is also used to synthesize sulfur-containing vitamins (thiamin, biotin, and lipoic acid).[8] Several enzymes, including those involved in protein synthesis, are activated by potassium. Magnesium is required for the activity of many enzymes, especially phosphate transfer and functions to stabilize ribosomes, cell membranes, and nucleic acids. Calcium acts to stabilize bacterial spores against heat and may also be involved in cell wall stability. Sodium is required by some but not all microorganisms and is present in a microorganism's environment.[8]

Additional micronutrients commonly required by microorganisms include iron, zinc, copper, cobalt, manganese, and molybdenum. These metals function in enzymes and coenzymes. These metals (except for iron) are also considered heavy metals and are toxic to microorganisms.

Liebig's law is the best way to understand how these compounds can be both nutrients and possibly toxic.

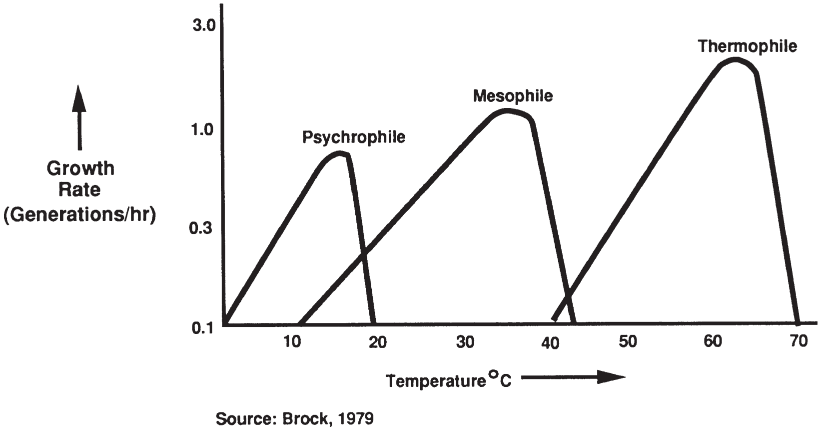
All of these factors are necessary to maintain a microorganism's metabolic processes. One part of any biological design is to provide the nutrients that are required by the microorganism. Once again, the carbon source should be left as the limiting factor in the biochemical reaction.

Environmental Factors

Several environmental factors can also affect biochemical reactions. These factors can control the type of bacteria that are prominent in the degradation of organics and will affect the rate of degradation. The main environmental effects are temperature, water, and pH. We will also review the different factors that can lead to toxic or inhibiting conditions.

Temperature

Temperature is an important microorganism growth factor. As the temperature rises, chemical and enzymatic reaction rates in the cell increase. However, proteins, nucleic acids, and cellular components will become inactivated if the temperature becomes too high. For every organism, there is a minimum temperature below which growth no longer occurs, an optimum temperature at which growth is most rapid, and a maximum temperature above which growth is not possible. The optimum temperature is always nearer the maximum temperature than the minimum. Temperature ranges for microorganisms are very wide. Some microorganisms have optimum temperature as low as 5 to 10 degrees Celsius (°C) (40 to 50 degrees Fahrenheit [°F]) and others as high as 75 to 80°C (167 to 176°F). The temperature range in which growth occurs ranges from below freezing to boiling. No single microorganism will grow over this entire range. Bacteria are frequently divided into three broad groups as follows: (1) thermophiles, which grow at temperatures above 55°C (131°F); (2) mesophiles, which grow in the midrange temperature of 20 to 45°C (68 to 113°F); and (3) psychrophiles, which grow well at 0°C (32°F). In general, the growth range is approximately 30 to 40 degrees for each group. Microorganisms that grow in terrestrial and aquatic environments grow in a range from 20 to 45°C (68 to 113°F). Figure 3-4 depicts the relative rates of reactions at various temperatures. As can be seen in Figure 3-4, microorganisms can grow in a wide range of temperatures. When designing a biological treatment system, the particular temperature



Source: Brock, 1979

FIGURE 3-4. Relationships of temperature to growth rate of a psychrophile, a mesophile, and a thermophile.

is not as important as ensuring that large temperature swings do not occur during the project. Changes in temperature will cause a change in population, and the new population will have to go through growth from small numbers present when the temperature became optimum for them.

Water

Water may be the most important factor influencing microorganism growth. Water quantity and quality varies in different environments. Water transports nutrients to the cells, aids the catalyst of many enzymes, and maintains the turgidity of the cell (osmotic pressure). The availability of water to microorganisms can be expressed in terms of water activity, which is related to the vapor pressure of water in the air over a solution (relative humidity). Water activity in freshwater and marine environments is relatively high and lowers with increasing concentrations of dissolved solute.[8] Bacteria can grow well in the salt water of an ocean (or 3.5 percent dissolved solids). Therefore, groundwater (even from a brine aquifer) will not pose any problems for bacterial growth.

When a microorganism grows in an environment with low water activity (high solute content or low moisture content), the cell must expend energy to extract water from solution. This usually results in a lower growth rate. This is most prevalent with microorganisms growing in soil or exposed to air. Below a certain water activity (0.60 to 0.70), microbial activity will cease and, unless the organism is resistant to desiccation, will die. Bacterial spores and sexual spores of fungi and algae are resistant to drying and can remain dormant for long periods of time. When water is reintroduced, microbial activity is reestablished.

pH

Microorganisms have ideal pH ranges that allow growth. Within these ranges, there is usually a defined pH optimum. Generally, the optimal pH for bacteria is between 6.5 and 7.5, which is close to intracellular pH. A bacterial cell contains approximately 1,000 enzymes, and many are pH dependent.[3] Most natural environments have pH values between 5 and 9. Only a few species can grow at pH values less than 2 or greater than 10.[8] In environments with pH values above or below the optimal level, bacteria are capable of maintaining an internal neutral pH by preventing hydrogen ions (H^+) from leaving the cell or by actively expelling H^+ as they enter. Once again, the most important factor with pH is to not allow major variations in pH during the project. The breakdown products of most compounds employed by the microorganisms as a food source or electron donor/acceptor will change the pH as they degrade. When carbon compounds are degraded under aerobic conditions, the pH is lowered due to the formation of carbonic acid (since carbon dioxide is generated by the microorganisms). When carbon compounds are degraded under anaerobic conditions, fermentative bacteria produce volatile fatty acids that lower the pH. However, once methanogenesis is established, the pH is typically buffered from change by the formation of ammonia and carbon dioxide. Nitrate degradation will generally decrease the pH. Thus, any biological reaction needs to be monitored for changing pH levels as the remediation progresses.

Toxic Environments

Many factors can render an environment toxic to microorganisms. Physical agents, such as high and low temperatures, sound, radiation, and hydrostatic pressure, can impact microbial growth. Chemical agents, such as heavy metals, halogens, and oxidants, can also inhibit microbial growth. This section briefly discusses how these factors influence microbial growth.

As previously mentioned, high temperatures will inactivate enzymes and denature microbial proteins. This will stop enzymatic reactions, weaken or rupture cell walls, and cause leakage of nucleic acids. Low temperatures will slow or stop cellular activity. Freezing prevents microbial growth but does not always kill the organism. When cells are subjected to freezing temperatures, their cytoplasm does not freeze as fast as the surrounding environment. The rate of temperature change will result in the formation of ice crystals. Ice crystals trigger an increase in the concentration of solutes in the water left within the cell, effectively causing dehydration. Many organisms do not survive because of dehydration. Ice crystal formation can also damage intracellular components, especially the plasma membrane, causing cellular death.[8]

Sound and radiation are not typically important factors with respect to environmental remediation. However, sound in the ultrasonic range can cause cavitation within cells, disrupting cellular function.[12] Radiation in the UV and short x-rays will cause the disruption of cellular activity. UV light will transform cellular deoxyribonucleic acid (DNA), preventing successful replication. X-rays are absorbed and convert molecules and atoms into ions that can break molecular bonds.[12]

Hydrostatic pressure can affect microbial growth. Hydrostatic pressure affects the activity of most enzymes, protein synthesis, and membrane transport. Most bacteria isolated from shallow water or soil grow best at atmospheric pressure and are inhibited or killed at hydrostatic pressures of 200 to 600 atm.[8]

Chemical agents, such as heavy metals and halogens, can disrupt cellular function by interfering with protein function. Mercury ions combine with the sulfhydryl (SH) groups in proteins; silver ions will precipitate protein molecules; and iodine will iodinate proteins containing tyrosine residues, preventing normal cellular function. The effects of various metals in soil has been described[13] and is affected by the concentration and pH of the soil. Oxidizing agents, such as chlorine, ozone, and hydrogen peroxide, oxidize cellular components, destroying cellular integrity. The oxidation and destruction of cells is possible with concentrations of hydrogen peroxide of five percent or greater.

Bacteria can adapt to many toxic environments. As with other environmental factors, changes in concentration will have a more severe effect on the bacteria than a constant concentration. When remediating a spilled material, therefore, it is important to know how long the material has been at the site. New spills will have a devastating effect on the natural bacterial population. (This is one of the times when specialized bacteria can be an important tool during the remediation.) Old spills will probably have bacteria that have adapted to the spilled material. When the remediation approach requires aboveground equipment, it is important to let the bacteria adjust to the organics and environment of the reaction tank. If you are cleaning two different areas at a site, with two distinct organics and environmental factors, it is important to remember that you cannot simply switch between the two feed sources. The bacteria will need time to adjust to either resulting environment.

Microbial Biodegradation of Xenobiotic Organic Compounds

The susceptibility of a xenobiotic compound to microbial degradation is determined by the ability of the microbial population to catalyze the reactions necessary to degrade the organics. Readily degradable compounds have existed on earth for millions of years; therefore, there are organisms that can mineralize these compounds. Industrial chemicals have been present on earth for a very short time on the evolutionary timescale. Many of these compounds are degradable, but many are persistent in the environment. Some xenobiotic compounds are very similar to natural compounds, and bacteria will degrade them easily. Other xenobiotic compounds will require special biochemical pathways in order to undergo biochemical degradation.

A few definitions would be helpful here in order to understand different levels of biological reactions. *Biodegradation* means the biological transformation of an organic chemical to another form with no extent implied.[14] Biodegradation does not have to lead to complete mineralization. *Mineralization* is the complete oxidation of an organic compound to carbon dioxide. *Recalcitrance* is defined as inherent resistance of a chemical to any degree of biodegradation and persistence to mean that a chemical fails to undergo biodegradation under a defined set of conditions.[15] This means that a chemical can be degradable, but because of the environmental conditions, the compound(s) may persist in the environment. With proper manipulation of the environmental conditions, biodegradation of these compounds can be demonstrated in laboratory treatability studies and transferred to field implementation.

As described above, microorganisms contain enzyme systems that are capable of cleaving the C–H bonds of an organic compound. However, many xenobiotic compounds are not structurally capable of immediately entering microbial biochemical pathways and must be modified. Compounds such as alkanes, saturated ring structures, and unsubstituted benzene are biochemically inert and must be oxygenated before dehydrogenation reactions can occur.[14] Bacteria contain oxygenase enzymes that are capable of reacting molecular oxygen with organic compounds and producing fragments that can then enter the normal metabolic pathways.

Gratuitous Biodegradation

Enzymes are typically described as proteins capable of catalyzing highly specific biochemical reactions. Enzymes are more specific to organic compound functional groups than to specific compounds. As Grady[14] described, an enzyme will not differentiate between the carbon–carbon (C–C) bond in a benzene molecule and the C–C bond in a phenol molecule. The functional capability of enzymes depends on the specificity exhibited toward the organic compound. A major enzymatic mechanism used by bacteria to degrade xenobiotic compounds has been termed gratuitous biodegradation and includes existing enzymes capable of catalyzing a reaction toward a chemical substrate.

For gratuitous biodegradation to occur, the bacterial populations must be capable of inducing the requisite enzymes specific for the xenobiotic compound. Oftentimes, this occurs in response to similarities (structural or functional groups) with naturally occurring organic chemicals. For example, a bacterium is producing the enzymes for benzene degradation. Chlorobenzene is introduced and is not recognized by the bacterium (its presence will not induce an enzyme to be produced). However, the enzymes already produced for benzene will also catalyze the degradation of chlorobenzene.

The capability of bacterial populations to induce these enzymes depends on structural similarities and the extent of substitutions on the parent compound. Generally, as the number of substitutions increases, biodegradability decreases unless a natural inducer is present to permit synthesis of required enzymes. To overcome potential enzymatic limitations, bacteria populations often induce a series of enzymes that coordinately modify xenobiotic compounds. Each enzyme will modify the existing compound so that a different enzyme may be specific for the new compound and capable of degrading it further. Eventually, the original xenobiotic compound will not be present, and the compound will resemble a natural organic compound and enter into normal metabolic pathways. This concept of functional pathways is more likely to be completed through the combined efforts of mixed communities rather than by any single species.

Cometabolism

Cometabolism has recently been defined as "the transformation of a nongrowth substrate in the obligate presence of a growth substrate."[14] A nongrowth substrate cannot serve as a sole carbon source that provides energy to support metabolic processes. A second compound is required to support biological processes, allowing the transformation of the nongrowth substrate. This requirement is added to make a distinction between cometabolism and gratuitous biodegradation.

Grady[14] present an example to clarify the distinction between cometabolism and gratuitous biodegradation. Consider a situation in which a culture of cells includes enzymes that are capable of catalyzing the degradation of a xenobiotic compound. Gratuitous biodegradation occurs if the xenobiotic compound added to the pregrown culture of cells transforms. (Remember, this is gratuitous biodegradation. The culture could not grow, and transformation would eventually cease.) Cometabolism occurs when energy is required to complete the transformation of the xenobiotic compounds. The xenobiotic compounds added to the pregrown culture would not transform because the culture could not extract energy from the substrate. Only when an energy-yielding substrate is added to the culture would transformation occur. Table 3-3 provides several examples of cometabolite compounds.

TABLE 3-3 Organic Chemicals Modified by Cometabolism

Acenaphthalene
Alkyl benzene sulfonate
Anthracene
Benzene
bis(4-Chlorophenyl) acetic acid
Butane
1-Butene
cis-2-Butene
trans-2-Butene
n-Butylbenzene
n-Butylcyclohexane
Carbon monoxide
3-Chlorobenzoate
4-Chlorotoluene
Cumene
Cyclohexane
Cycloparaffins
p-Cymene
DDT
n-Decane
1,2-Diethylbenzene
Diethyl ether
9,10-Dimethylanthracene
1,3-Dimethylnaphthalene
2,3-Dimethylnaphthalene
1,6-Dimethylnaphthalene
2,7-Dimethylnaphthalene
Dodecane
Ethane
Ethene
Ethylbenzene
Heptadecane
Hexadecane
4-Isopropyltoulene
Limonene
2-Methylanthracene
2-Methylnaphthalene
3-Methylphenanthrene
Naphthalene
Octadecane
Pentadecane
Phenylcyclohexane
Propane
Propene
n-Probylbenzene
Retene
Tetradecane
Thianaphthene
Toluene
2,4,5-Trichlorophenoxyacetate
Tridecane
1,2,4-Trimethylbenzene
Undecane
m-Xylene
p-Xylene

Source: Dragun 1988.

Microbial Communities

Complete mineralization of a xenobiotic compound may require more than one microorganism. No single bacterium within the mixed culture contains the complete genome (genetic makeup) of a mixed community. The microorganisms work together to complete the pathway from organic compound to carbon dioxide. These associations have been called consortia, syntrophic association, and synergistic associations and communities.[14] We need to understand the importance of the community when we deal with actual remediations. Conversely, we need to understand the limitations of laboratory work with single organisms. This work does not represent the real world of degradation. Reviewing the strengths of the communities will also reveal the limitations of adding specialized bacteria that have been grown in the laboratory.

Community Interaction

Microbial communities are in a continuous state of flux and constantly adapting to their environment. Population dynamics, environmental conditions, and growth substrates continually change and impact complex interactions between microbial populations. Even though environmental disturbances can be modified by microorganisms, microbial ecosystems lack long-term stability and are continually adapting.[14] It is important to understand the complexities and interactions within an ecosystem to prevent failure when designing a biological system.

The existence of specific microbial interactions within communities is difficult to prove and has prompted investigators to classify members of communities on a functional basis. Organisms that degrade xenobiotic compounds have been divided into two groups: the primary utilizers and the secondary organisms.[14, 15] The primary utilizers are those species capable of metabolizing the sole carbon and energy source provided to the system. The secondary organisms cannot use the major substrate and rely on the products generated by the primary utilizers.

Communities and Adaptation

Mixed communities have greater capacity to biodegrade xenobiotic compounds because of the greater genetic diversity of the population. Complete mineralization of xenobiotic compounds may rely on enzyme systems produced by multiple species. Community resistance to toxic stresses may also be greater because of the likelihood that one of the organisms in the community can detoxify the ecosystem.

Community adaption is dependent on the evolution of novel metabolic pathways. As described by Grady,[14] a bacterial cell considered in isolation has a relatively limited adaptive potential, and adaption of a pure culture must come from mutations. Mutations are rare events. These mutations are generally responsible for enzymes that catalyze only slight modifications to the xenobiotic compound. An entire pathway can be formed through the cooperative effort of various populations and occurs because there is a greater probability that an enzyme system capable of gratuitous biodegradation exists within a larger gene pool. This genetic capability can then be transferred to organisms lacking the metabolic function that enhances the genetic diversity of the population. Through gene transfer, individual bacteria have access to a larger genetic pool, allowing the evolution of novel degradative pathways.

Genetic Transfer

Genes are transferred throughout bacterial communities by three mechanisms: conjugation, transformation, and transduction.[8, 10, 12, 14, 21] Conjugation appears to be the most important mechanism of gene transfer in the natural environment. Conjugation involves the transfer of DNA from one bacterium to another while the bacteria are temporarily joined. The DNA strands that are transferred are separate from the bacterial chromosomal DNA and are called plasmids.[8, 10, 12, 21] Plasmids exist in cells as circular, double-stranded DNA and are replicated during transfer from donor to recipient. Unlike chromosomal DNA that encodes for life-sustaining processes, plasmid genes encode for processes that enhance growth or survival in a particular environment. Examples of functions that are encoded on plasmids include antibiotic resistance, heavy metal resistance, and certain xenobiotic degradation (i.e., toluene).[21]

Plasmids are not necessarily species specific, which allows the successful transfer of genetic material from many different species of the microbial community.[21] Transposons, which are smaller DNA fragments, are also able to be transferred. These fragments incorporate into the viral DNA, plasmids, and chromosomal DNA of bacteria. Therefore, genes that have entered one cell type as transposons may eventually enter another cell type after being transported into it as a plasmid, minimizing transfer barriers among the community.[14] There are limitations to the interspecies and intraspecies transfer of genetic material. These limitations are influenced by the environment, stability between the mating pair, and contact time between the donor and recipient.[8, 10, 12, 21]

Degradation Rate

Microbial degradation of organic material is generally described as the time necessary to transform the substrate from its original form to another form. The final form can be a structurally different compound or the complete mineralization into carbon dioxide, water, oxygen, and other inorganic matter. Biodegradation rates can be measured by the loss of the original substrate, the consumption of oxygen, or the evolution of carbon dioxide or methane.

Biodegradation rates can be described by two reaction rates,[3, 13, 16] which are called zero order and first order. Reactions that transform the substrate and are unaffected by changes in the substrate concentration are called zero-order kinetics.[3, 13, 16] In these cases, the reaction rate is determined by some factor other than the substrate concentration. For example, if the cell density is so great that the quantity of substrate is insufficient to support a significant increase in cells, the kinetics of the disappearance of organic compounds present is zero order (linear with time).

First-order reactions occur when the biodegradation rate of a substrate is proportional to the concentration of the substrate. This reaction has been demonstrated in the literature for the biodegradation of many organic compounds.[13] First-order kinetics described for a single bacterial species includes two patterns. In the first pattern, there is no appreciable increase in cell numbers. The bacteria have reached a threshold or the initial cell number is too large, relative to the quantity of organic compound, to permit an appreciable increase in bacteria. At constant biomass or severely limiting substrate levels, the degradation rate is proportional to the concentration of residual substrate, which falls off continually. In the second pattern, few active cells are initially present, and the chemical concentration is above any threshold concentration that may limit the degradation rate. Under these conditions, the bacteria will grow but at a rate that falls constantly with the diminishing and always limiting substrate concentration.

In the real world, the reaction rates can change during the project. For these situations, hyperbolic rate law or the Monod equation describes the growth of a microorganism population as a function of substrate level over a range of concentrations. This function is dependent on substrate concentration and the growth rate of the microorganisms, and it is particularly useful when the initial concentration is in the

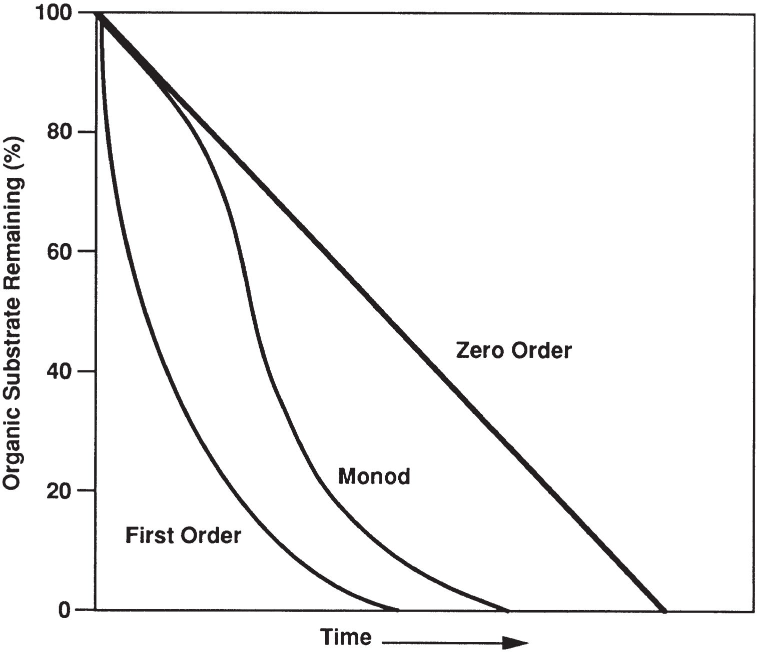


FIGURE 3-5. Disappearance curves based on various kinetic models.

mixed-order region. Figure 3-5 summarizes the various growth rate models.

One final area needs to be discussed under degradation rate: low concentrations. We normally think of treatment process efficiency in terms of percent removal. However, biological systems cannot always be evaluated based on percent removal. At low concentrations, diffusion of the compounds to the cell surfaces may not be sufficient for growth or maintenance of the microbial populations. This concentration at which biological activity is reduced is called the threshold and is controlled by the substrate concentration and diffusivity. No matter what the influent concentration, the biological reaction may not continue past this threshold value. Therefore, percent removal is not always a good measurement to describe the performance of a biological system. This is especially true for the low concentrations we normally find with groundwater contamination.

This natural limitation in the bacterial reaction rates forces us to develop additional methods to measure the performance of biological reactors. Two other methods for evaluation could be influent and effluent concentrations. Biological systems require a minimum amount of food to replace the bacteria that are lost to decay and washout. A biological reactor efficiency can be measured by the influent concentration required to maintain a viable population.

Effluent concentration is also an important measurement. Will the reactor design achieve an effluent concentration equal to the natural threshold level of the organic compound? Will the reactor be able to achieve concentrations below the threshold level? Finally, concentration thresholds may also help to explain the persistence of low concentrations of biodegradable compounds in the environment. When a remediation reaches the low parts per billion (ppb, equivalent to µg/L) level in the aquifer, even degradable compounds may be very slow to reach final concentrations. Bacteria may have a limited effect on these compounds at these concentrations.

Degradative Mechanisms

We have discussed how the degradation of different organic compounds requires different enzymes and that different microorganisms are required for specific degradation. However, all degradation is related. One degradation pathway is central to all microorganisms. The pathway by which organic compounds are oxidized to release energy or used as a substrate to form cellular components is called the tricarboxylic acid cycle, Figure 3-6. The key compound in the tricarboxylic

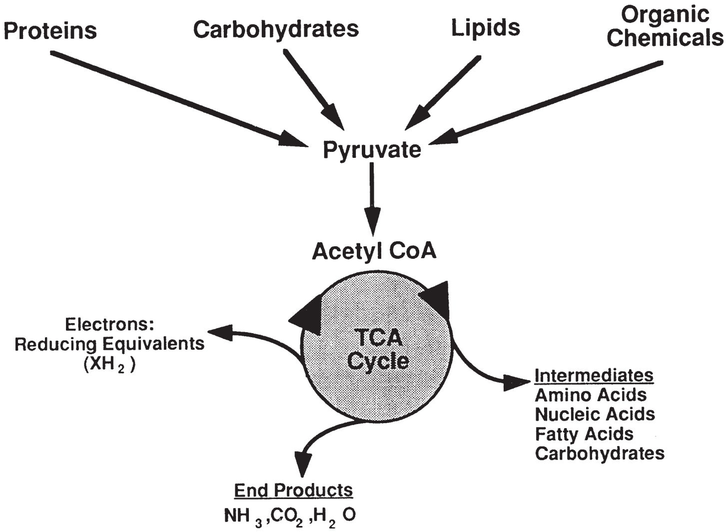


FIGURE 3-6. TCA cycle.

acid cycle is acetyl-CoA (an acetyl radical coupled to coenzyme A) derived from pyruvate. Acetyl-CoA binds to oxalacetate to form citric acid, which continues through the cycle producing carbon dioxide, nicotinamide adenine dinucleotide (an adenosine triphosphate formation), and two intermediates (α-ketoglutarate and oxalacetate) used in amino acid synthesis.

Bacteria degrade compounds because they recognize them as food, not because they are doing us a favor. The degradation of xenobiotic compounds is dependent on the capability of deriving energy or biosynthetic fragments from the compound. The objective of the enzymes that we are trying to induce is to get the xenobiotic compound into the tricarboxylic acid cycle. If the enzymes are induced and the reactions proceed, the products are then readily metabolized by the organism's biochemical pathways. All microorganisms use the tricarboxylic acid cycle. Only the pathways to the tricarboxylic acid cycle differ.

Many different pathways are available depending on the compound that is being degraded. The following sections are some examples of the degradation mechanisms of several types of organic compounds.

Aliphatic Hydrocarbons

Several microorganisms are capable of degrading aliphatic hydrocarbons.[8, 12, 13, 17] These reactions are strictly aerobic. These compounds represent a large percentage of the compounds found in petroleum hydrocarbons.

Figure 3-7 is a summary of the degradation of *n*-octane. The initial step involves the reaction of molecular oxygen with one of the carbon molecules of the hydrocarbon. Monoxygenases are most generally involved and bind oxygen to the terminal methyl group or the second carbon. Subsequent reactions form fatty acids that can be incorporated in the cell or can be further oxidized by β-oxidation (fatty acid oxidation).[8]

Cyclic Hydrocarbons

The degradation of cyclic hydrocarbons is similar to the degradation mechanism of aliphatic hydrocarbons. The products of degradation are further degraded by β-oxidation.[13] The degradation of cyclic hydrocarbons with functional groups becomes more complicated because more than one reaction is available. Figure 3-8 shows the pathway for the degradation of cyclohexane to an aliphatic, and Figure 3-9 shows the degradation of cyclohexane to carboxylic acid.

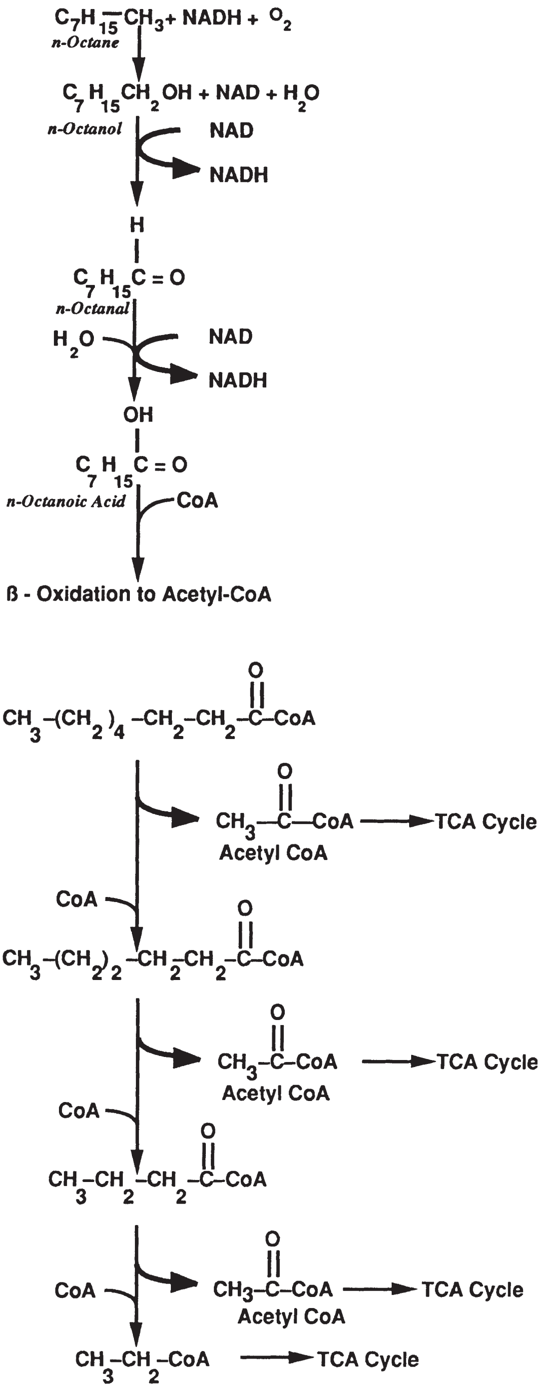
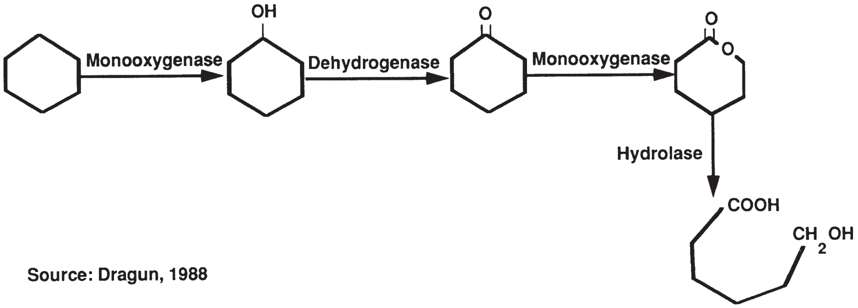
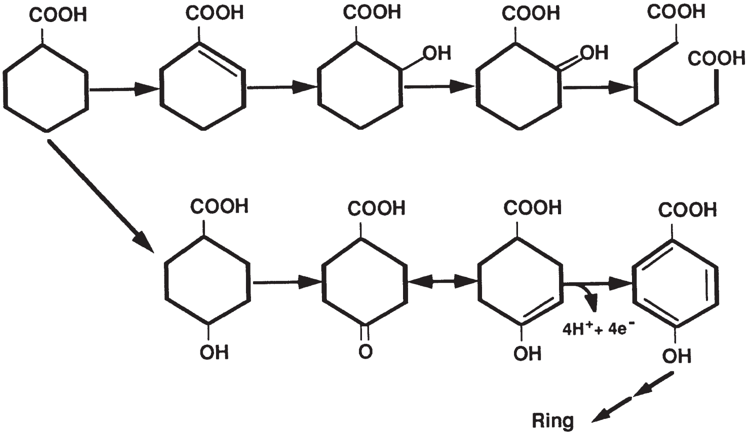


FIGURE 3-7. Degradation of *n*-octane.



Source: Dragun, 1988

FIGURE 3-8. Degradation of cyclohexane to an aliphatic hydrocarbon.



Source: Dragun, 1988

FIGURE 3-9. Degradation of cyclohexane to carboxylic acid.

Aromatic Hydrocarbons

Aromatic hydrocarbon degradation involves dioxygenases. The product formed is catechol, a dihydroxybenzene that is broken down leading to either acetyl-CoA or tricarboxylic acid intermediates. Several aromatic compounds possessing one or more six-carbon rings, such as benzoic acid, ethylbenzene, phthalic acid, phenanthrene, naphthalene, anthracene, toluene, phenol, and naphthol, follow similar degradative pathways.[18] Figure 3-10 shows the degradation pathway for an aromatic hydrocarbon.

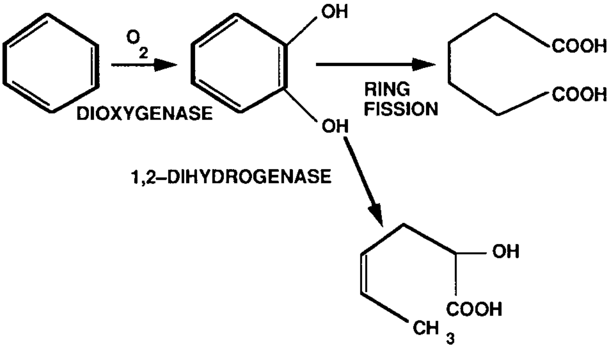
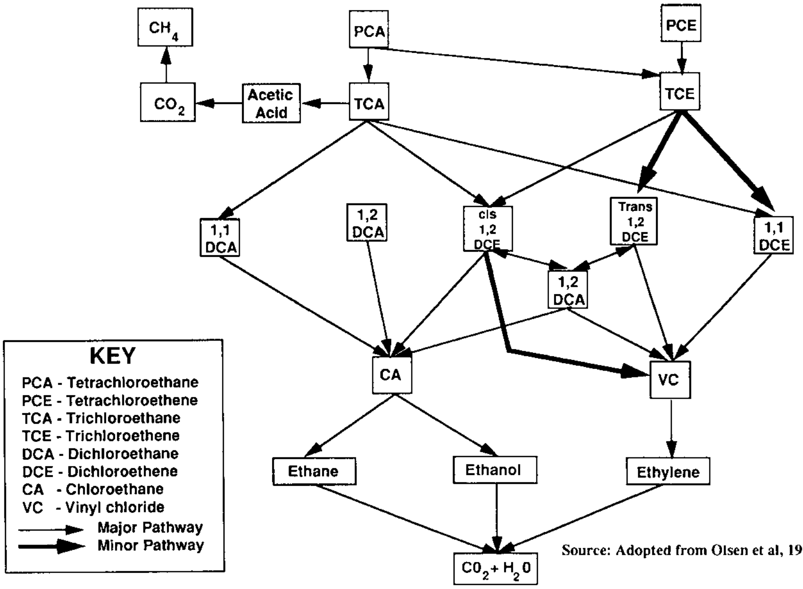


FIGURE 3-10. Degradation of an aromatic hydrocarbon.

Halogenated Hydrocarbons

Many pathways are available for the degradation of halogenated hydrocarbons. Some of the compounds degrade under anaerobic conditions. Some require a cometabolite for degradation. Many investigators have reported the mechanism of halogenated hydrocarbon transformation. Figure 3-11 is a compilation of several investigators' research into the degradation of common halogenated hydrocarbon pollutants.[19, 22, 23, 24, 25, 26, 27, 28]



Source: Adopted from Olsen et al, 1990

FIGURE 3-11. Transformations of a chlorinated aliphatic hydrocarbons.

BIOLOGICAL REACTORS FOR CONTAMINATED WATER

Now that we have a better understanding of how biochemical reactions take place and how to degrade xenobiotic compounds, we need to explain how to use these mechanisms for the treatment of contaminated groundwater. The first point to make about biological reactors is to establish the difference between a biological reaction and a biological reactor. The biological reaction is bacteria producing requisite enzymes to use a specific contaminant as a food and energy source. In other words, is the compound degradable? The biological reactor is designed to maximize the biological reaction in an economic manner. The reactor design solves specific problems that are encountered with the contaminated streams that are being considered.

We must remember that the bioreactor designs that are available today were originally developed for the treatment of municipal wastewater (e.g., sanitary wastewater). Municipal wastewater is generally characterized as having moderate to high TSS concentrations and a relatively low concentration of soluble and insoluble organics, as measured by biochemical oxygen demand (BOD). Municipal wastewater BOD concentrations are typically 150 to 300 mg/L. Many of the challenges encountered in the biological treatment of municipal wastewater are not encountered in groundwater sources:

- *Large fluctuations in hydraulic, solids, and organic loading (e.g., the sanitary waste generated is much lower during the evening when the majority of the population is asleep).* In most groundwater treatment applications, the flow rate and contaminant concentrations are fairly stable (generally varying by 25 percent or less).
- *Significant quantity/concentration of inorganic or inert solids (e.g., rags, plastics, leaves, etc.) that must be removed prior to the bioreactor.* Typically, groundwater TSS concentration is low (typically less than 100 mg/L) and stable, consisting of aquifer solids such as fine-grain sands and silts from the geologic formation. However, if the groundwater is contaminated with high concentrations of degradable organics, the resulting environment in the aquifer will be anoxic and/or reducing. Under these conditions, geological compounds can dissolve into the groundwater. This will typically increase the hardness of the water (calcium and magnesium) and increase the concentration of iron. All of these compounds have the potential to form scale deposits (depending on pH) in the groundwater extraction wells, conveyance piping systems, and tanks. This

means that the designer has to pay close attention to the natural compounds in the aquifer, as well as the contaminants.

- *Presence of coliform bacteria and similar organisms that require disinfection operations prior to discharge.* These organisms are not an issue with groundwater unless the aquifer has been impacted by infiltration from a sanitary sewer system.

Therefore, biological treatment of groundwater does not require the significant (and expensive) equalization processes and solids removal pretreatment processes associated with municipal wastewater treatment. Because groundwater treatment systems typically do not include human or animal waste streams, state and federal regulations requiring disinfection (e.g., Clean Water Act–Part 40.133 of the Code of Federal Regulations) will not be applicable in most cases. It may be feasible to convey groundwater directly to a bioreactor. Thus, when it is determined that the biological reaction can occur, we have to use a biological reactor design that addresses the problems associated with groundwater as we analyze the applicability of bacteria for our groundwater problem.

There are three basic challenges to be solved in the design of aerobic and anaerobic biological reactors. The first is contact between the bacteria and the organic contaminants. The second is retention of a sufficient biomass inventory within the bioreactor to facilitate the desired degradation of the contaminant load. A third challenge for aerobic bioreactors only is oxygen transfer to the bacteria. We can compare the various biological reactor designs that are available based on how they solve these challenges. Other criteria will also be used to establish the advantages and disadvantages of specific reactor designs for groundwater, but bacterial contact, biomass inventory, and oxygen transfer are the three functions that are the most common to bioreactor designs.

Bacterial contact is more than simply mixing the bacteria with the organic contaminants. The goal of the biological reaction is to destroy a maximum amount of the organics and leave a minimum concentration of the contaminants remaining in the water. To achieve these goals, the biomass must be in contact with the organics and have extended periods of time to complete the biochemical reactions. In other words, the organics must have sufficient time in the reactor. This concept is most commonly referred to as liquid residence time, or hydraulic retention time. Figure 3-12 shows the relationship between the effluent organic concentration and the liquid residence time of the groundwater.

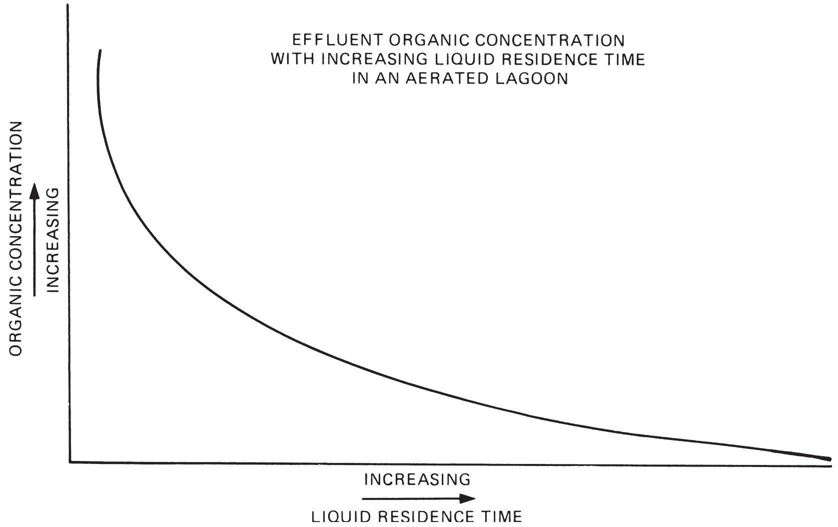


FIGURE 3-12. Effluent organic concentrations with increasing liquid residence time.

In addition to bacterial contact and hydraulic retention time, there must be a sufficient quantity of bacteria (e.g., biomass) within the bioreactor to facilitate conversion of the organics to meet or exceed the treatment goal within the constraints of the hydraulic retention time. This is referred to as the biomass inventory within the bioreactor. The primary challenge associated with maintaining the required biomass inventory is providing the means to separate the bacteria from the treated effluent, either within the vessel itself or through an external process on the condition that the bacteria can be returned to the bioreactor.

Oxygen transfer does not affect the performance of the reactor design as long as a minimum oxygen concentration is maintained. Oxygen transfer is mainly related to the cost of biological treatment. For large wastewater treatment systems, oxygen transfer is a major consideration in the economics of the design. However, the original reason certain reactors were designed in a specific manner was to solve an oxygen transfer problem. To understand the differences between the reactors, we must understand the original design criteria.

Biological reactors can be separated into two main groups: suspended growth reactors and fixed-film reactors. With suspended growth reactors, the bacteria are grown in the water and are thoroughly mixed with the organics in the water. Fixed-film systems grow bacteria on an inert support medium. The water containing the organics passes over the film of bacteria. All of the designs have advantages and disadvantages in their applications to groundwater treatment.

Suspended Growth Reactors

Suspended growth bioreactors are one type of ex situ biological treatment system used to biologically degrade organic constituents in groundwater under aerobic conditions (suspended growth anaerobic bioreactors are typically mechanically mixed lagoon systems, but their applications for groundwater treatment are very limited and will not be further discussed). Suspended growth bioreactors use diverse microbial populations (biomass) that are freely suspended in an aqueous solution. The biomass converts soluble, colloidal, and particulate biodegradable organic matter into new cell mass and innocuous end products such as carbon dioxide and water. There are several different types of suspended growth bioreactors: complete mix, plug flow, oxidation ditch, aerated lagoons, extended aeration, contact stabilization, sequencing batch reactors, and membrane reactors.

A suspended growth bioreactor system requires a reactor vessel or multiple vessels for flexibility, an oxygen source, mixing equipment to ensure the bacteria are kept in constant suspension and in contact with the contaminants (note that most aeration technologies achieve oxygen transfer and complete mixing simultaneously), and a means to separate biomass from treated effluent. The liquid content of the bioreactor, composed of water, biomass, organic solids, inert solids, etc., is referred to as mixed liquor and, more commonly, as activated sludge. Mixed liquor suspended solids (MLSS) refers to the solid portion of the mixed liquor, which is made up of organic (volatile) and inorganic/inert (nonvolatile) components. The volatile portion of the MLSS, denoted as mixed liquor volatile suspended solids (MLVSS), consists mainly of biomass (living and dead microorganisms).

Management of the solids inventory in the suspended growth bioreactor is of major importance to treatment effectiveness. The most important component of the solids management is maintaining a sufficient biomass inventory to convert the dissolved organics in the groundwater to water, carbon dioxide, and more biomass at a rate that meets or exceeds the design treatment goal. Each suspended growth bioreactor type employs a method to separate the mixed liquor from the treated effluent either within the vessel (e.g., sequencing batch reactors, certain membrane bioreactor technologies) or in a downstream process (e.g., clarifier, membrane system) to be returned to the bioreactor.

Biomass inventory is determined by the number and variety of microorganisms in the MLVSS. Microorganisms that settle and thicken well (referred to as floc forming) include a mixture of bacteria, protozoa, and some metazoa. In a well-maintained system, these microorganisms will make up the majority of the population in the suspended growth bioreactor (in most groundwater applications, rod-shaped bacteria will predominate). Microorganisms that do not settle and thicken well are considered nuisance organisms, usually consisting of filamentous biomass. While some filamentous biomass can help flocs stick together, an overabundance will create bulking and prevent biomass compaction. Some causes of filamentous biomass taking over a population include low dissolved oxygen, low organics relative to biomass inventory, nutrient deficiency, and low pH.

MLSS concentration ranges for typical municipal activated sludge processes are 1,500 to 3,000 mg/L. MLSS concentration for groundwater applications range from 1,500 to 10,000 mg/L, depending on the presence of dissolved iron and other metal species that can form precipitates within the bioreactor and aquifer solids.

Important information can be gained from observing the color of the mixed liquor. Mixed liquor in a healthy system will be brownish in color with a small amount of crisp, white foam present on the surface of the reactor. A black color, or the presence of a rotten egg odor (hydrogen sulfide), indicates insufficient aeration (low dissolved oxygen).

Mean Cell Residence Time (Sludge Age)

Sludge age is defined as the mean cell residence time (MCRT) or the solids retention time, which is the inverse of the specific growth rate of the bacteria. It can be considered the time the active biomass is reproducing and degrading organics within the system. Sludge age is controlled by the loss of bacteria as a result of the wasting rate of the settled bacteria (either from a clarifier or membrane bioreactor blowdown) and by the uncontrolled loss of bacteria in the treated effluent. Theoretically, the longer the solids retention time is, the greater the substrate removal. The typical sludge age for conventional activated sludge ranges from five to fifteen days. The typical sludge age for groundwater applications ranges from ten to twenty days.

As discussed above, sludge age is an important parameter for the effectiveness of treatment since it effects the settling characteristics of the mixed liquor. Settleability is an important consideration for all suspended growth technologies that rely on clarification to maintain the proper biomass inventory. The following is a summary of problems associated with sludge age:[38]

- Maintaining a sludge age that is too long (old sludge) can result in the proliferation of *Nocardia*, a filamentous bacterium. Overpopulation of *Nocardia* results in the accumulation of a thick, viscous brown foam (resembling chocolate mousse) on the surface of the basins.
- Old sludge can result in ashing and pin floc proliferation, poor settling conditions that result in limited clarifier effectiveness.
- Maintaining a sludge age that is too short (young sludge) can result in the presence of a voluminous, billowing white foam, which results from the production of surfactants by the rapidly growing bacteria.
- Young sludge can result in the proliferation of straggler floc and dispersed growth. Straggler floc particles are relatively large and are caused by a filamentous biomass that appears to be light, fluffy, and almost buoyant within the clarifier. Dispersed growth refers to biomass that is not floc forming, resulting in individual cells that do not settle and pass through the clarifier (exhibited by visible turbidity in the clarifier effluent).

Food to Microorganisms Ratio

The food to microoranisms ratio (F:M ratio) refers to the ratio of the organics available to be utilized by the microorganisms as “food” to the available microorganisms (biomass inventory). The F:M ratio is defined as the ratio of the total mass in pounds of BOD per day (lb BOD/day) to the total mass in pounds of mixed liquor volatile suspended solids (lb MLVSS). Typical F:M ratio values for groundwater applications range from 0.2 to 0.9 lb BOD/lb MLVSS/day. The high food to microoranisms ratio can be maintained because of the large quantity of inorganic solids in the mixed liquor. The inorganic solids increase the surface area, allowing more biomass to grow yet still efficiently settle out in the clarifier. When the biomass is attached to a surface, it also increases the efficiency by which it can metabolize the food.

Groundwater Applications

Suspended growth biological treatment has been successfully applied in the pretreatment (e.g., bulk removal of organics prior to discharging to a municipal wastewater treatment system for final treatment), as well as final treatment, of contaminated groundwater (e.g., "direct discharge" or discharge of treated effluent that meets prescribed regulatory limits under an appropriate permit to a surface water). It has been the author's experience that suspended growth biological treatment technologies are good candidates for pretreatment and treatment of groundwater with the following characteristics:

- Organic constituents that are degradable under aerobic conditions.
- Moderate to high organic loading: BOD concentrations of 75 mg/L or greater. If BOD data are not available, TOC concentrations of 125 mg/L or greater.
- Iron concentrations of 10 mg/L or greater.
- Alkalinity and hardness concentrations exceeding 500 mg/L.
- TSS concentrations greater than 50 mg/L (e.g., geologic formation containing fines).

Treatment using a suspended growth bioreactor requires a moderate to high concentration of organics to provide sufficient food sources to maintain the microbial population and maintain a stable microbial culture. Dissolved iron will precipitate in the presence of oxygen and form iron hydroxide. Iron hydroxide becomes complexed with water to form a large molecule that promotes the agglomeration of bacteria and other particulates (aquifer solids, carbonate precipitates, as well as other metals that precipitate) into flocs. This characteristic is extremely beneficial for suspended growth biological systems because better flocs result in more surface area of active biomass (increases the bacteria contact with organics), facilitating improved settling characteristics of the biomass (improving the efficiency at which the biomass can be separated from treated effluent and making it easier to maintain a sufficient biomass inventory). Certain compounds, such as sugars and alcohols, will degrade very quickly in a biological system. Other compounds require longer contact times with the bacteria to degrade. The easier a compound can be assimilated by the bacteria, the faster and more efficiently the bacteria can turn that compound into new bacteria. When compounds are persistent and hard to degrade (refractory compounds), the bacteria need a longer retention time to replace their lost numbers. The bacteria must first remove the easily degradable organics before they are willing to produce the enzymes necessary to degrade the refractory compounds. They must be a little hungry before they go after these organics.

The most often used types of suspended growth bioreactor systems for groundwater treatment are complete mix reactors (also known as "activated sludge" bioreactors), sequencing batch reactors, and membrane bioreactors. A complete mix system consists of one or multiple vessels in which the concentration of contaminants and suspended biomass (mixed liquor) remains constant throughout the tank, and mixing occurs instantaneously when contaminated groundwater enters the vessel(s). In this compartment/portion of the bioreactor, groundwater is continuously introduced, and treated effluent is continuously removed from the system with the mixed liquor. Therefore, a downstream process is required to separate suspended biomass from the treated effluent (gravity sedimentation by the clarifier in conventional complete mix systems and by membranes in membrane bioreactors) and returned to the bioreactor (refer to Figure 3-13). In a batch reactor, equalization, aeration, and clarification occur in a timed sequence using only one vessel. Membrane bioreactors employ membrane filtration to separate biomass from treated effluent, and sludge age is maintained by periodic blowdown of the mixed liquor. A more detailed description of each of these suspended growth bioreactor systems is included in the following sections.

Complete Mix/Activated Sludge Bioreactors

Activated sludge bioreactors (commonly referred to as aeration basins for the mechanism used to transfer oxygen and impart mixing) can also be classified as conventional, high-rate, or low-rate, which refers to the loading rate or organic feed rate of the system. Conventional activated sludge applies to complete mix systems with a food to microorganisms ratio of approximately 0.2 to 0.5 lb BOD/lb MLVSS/day. Low-rate activated sludge systems, characterized by the introduction of

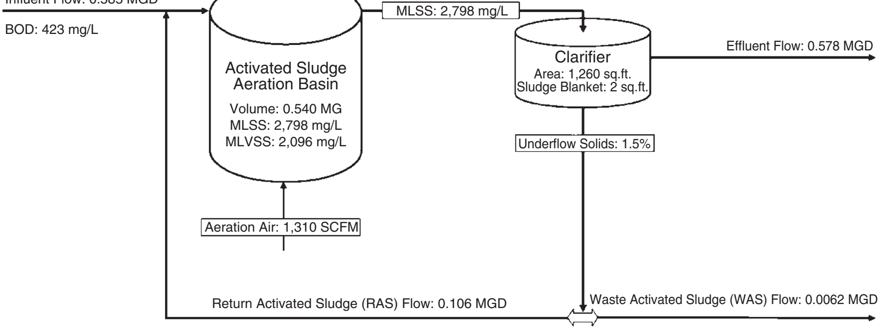


FIGURE 3-13. Example of a suspended growth bioreactor (activated sludge) system.

groundwater, with a long aeration time, high mixed liquor suspended solids concentration, high return activated sludge pumping rate, and low sludge wastage are generally not applied to groundwater treatment. High-rate activated sludge systems are characterized by a food to microorganisms ratio of 0.5 to 0.9 lb BOD/lb MLVSS/day, short hydraulic retention time, and high sludge recycle ratio.

Powdered activated carbon can be added to the aeration basin to enhance the suspended growth process. The addition of powdered activated carbon improves solids settling characteristics, increases the sludge's ability to dewater, and reduces odor and foaming issues. Powdered activated carbon can also improve the removal rate of organic constituents by absorbing organic and toxic substances within the system during peak loading rates. The powder activated carbon can remove slow degrading or nondegrading organic material from the water while the bacteria can attach to the powdered activated carbon and consume the organics that have absorbed to the carbon. The main advantage of the system is that it can treat a large variety of organic compounds. However, a key disadvantage of powdered activated carbon addition is the need to regenerate the carbon for reuse or to purchase virgin carbon for each use. In addition, tertiary filtration may be required to remove the powdered activated carbon from the waste stream.

Advantages

Activated sludge is the most widely used method of biological treatment in the wastewater treatment area. The basic advantages are that the process produces low effluent concentrations, the system can treat many organics at the same time, and the same equipment can be used for a variety of influent conditions.

Disadvantages

The main disadvantages are the cost of manpower to keep the system adjusted to the influent conditions, the relative cost of oxygen transfer compared to fixed-film systems, and the critical need to keep the bacteria in a growth stage in which their settling characteristics are at a maximum. If the bacteria do not settle properly, they will not be removed from the water stream in the clarification process and, therefore, will not be returned to the aeration basin as return activated sludge. To maintain the settling properties, two things are necessary: the environment in which the bacteria grow must not have any major changes, and the bacteria must be grown at the proper sludge age that promotes flocculation. In groundwater treatment, the influent has very little variation on a day-to-day basis. There is normally no need for equalization as there is in wastewater treatment. The main problems when using activated sludge with groundwater are the life cycle concentration and growing the bacteria in their flocculent stage during the entire project. It is important for the design engineer to design the activated sludge treatment system to be operable over as much of the life cycle as possible. Even with a good design, the activated sludge system will still require a relatively high level of operator attention to ensure that the system is operating in the correct manner.

Design

The design of activated sludge suspended growth bioreactors is often based on the loading rate of BOD in pounds per unit volume of the bioreactor (cubic feet). Table 3-4 summarizes typical process loading ranges for conventional activated sludge suspended growth bioreactors.

Sequencing Batch Reactors

In a single reactor, a sequencing batch reactors system accomplishes equalization, aeration, and clarification in a timed sequence (refer to Figure 3-14) in one vessel. In a conventional activated sludge process, however, multiple tanks are required to meet each step in the sequencing batch reactor process. The mixed liquor remains in the reactor during each phase of the sequencing batch reactor cycle. Each cycle of a sequencing batch reactor system consists of five steps: fill, react, settle, decant, and idle. During the fill stage, groundwater is distributed through the settled sludge, and biodegradation is initiated. The reactor is filled with contaminated water and can be aerated, depleted of oxygen, or a combination of both. During the react step, influent flow is terminated and aeration/mixing continue until biodegradation of the organic constituents in the groundwater is complete. Sludge

TABLE 3-4 Suspended Growth Bioreactor Design Summary

Loading Range	BOD Removal (%)	Sludge Age (days)	MLVSS/ MLSS	F:M Ratio (lb BOD/lb MLVSS/day)	Loading (lb BOD/ 1,000 cu ft/day)
High rate	50–95	1–3	>0.75	0.5–1.5	100–1,000
Groundwater w/ colloidal particulates	85–95	5–20	0.5–0.8	0.3–1.0	60–240
Groundwater	85–95	10–20	0.7–0.8	0.1–0.5	40–60
Conventional	85–95	5–15	>0.75	0.2–0.5	20–40
Low rate	85–95	20–30	>0.75	0.05–1.5	10–25

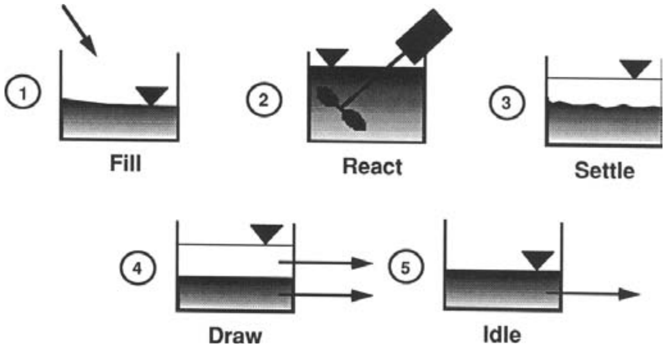


FIGURE 3-14. Sequencing batch reactor treatment stages.

wasting also occurs during the react step. Wasting during this phase ensures a uniform discharge of solids based on the mixed and aerated conditions in the reactor. During the settling step, the aeration/mixing are discontinued and quiescent conditions allow the biomass to settle. Clarified effluent remains above the sludge and is removed from the tank during the decant phase. During the idle stage, the reactor is waiting for the next fill stage. This phase allows a second sequencing batch reactor system to complete its fill stage and begin the react stage, increasing operational flexibility.

A sequencing batch reactor system typically includes a tank, aeration and mixing equipment, a decanter, pumps, piping and appurtenances, and a process control system that includes level sensors, timers, automatic switches, and valves that sequence and time the five different operations. A programmable logic controller can be used to automatically operate each phase of the sequencing batch reactor cycle. Decanters, which can be either floating or fixed, remove the clarified effluent from the reactor. The inlet to the floating decanter remains just below the water surface, minimizing the potential removal of solids in the effluent and offering the flexibility to vary the fill and draw volumes. Fixed decanters are built into the side of the tank and can be used provided that the settle stage is long enough to lower the sludge blanket below the inlet of the decanter. Extending the settling step will minimize the chance of solids flowing into the effluent.

Pairs of tanks are recommended for ease of operation and efficiency. While one reactor is accepting groundwater, the other reactor is going through the subsequent steps of metabolization, settling, and decanting. The reactors switch back and forth to maintain a constant influent flow rate. If a continuous feed system is used, a baffle wall can be provided to separate the influent from the decanter. The baffling directs the influent groundwater below the sludge blanket, preventing the contaminated groundwater from being directly discharged from the system. A separate sludge wasting system can be included to allow sludge to be wasted during the decant or idle phases instead of during the react phase.

The decant volume in each reactor is defined as the flow to the system divided by the total number of cycles completed by the system. The decant phase is typically half the time of the fill phase. Therefore, the rate of decanting the treated effluent must be twice as fast as the rate of fill to ensure enough volume within the reactor for the next cycle of operation. The maximum decant volume is defined as the difference between the minimum reactor sidewater depth and the maximum sidewater depth. The decanter will typically be controlled by the reactor's level sensor that will close the effluent valve on the decanter by sending an electrical signal at a predetermined water level.

The sequencing batch reactor system operates in time rather than space; therefore, it can be operated to simulate any conventional activated sludge process. The hydraulic retention time in a sequencing batch reactor system is dependent on the flow rate of groundwater into the system and the total volume of the reactor and can range from 3.5 to 7 hours or can be increased to 36 hours for an extended aeration system. Approximately 50 percent of each cycle is typically devoted to aeration, 25 percent to settling, and 25 percent to the decant step.

Advantages

The advantages of the sequencing batch reactor are its simplicity of operation, small footprint, flexible design, and ability to maintain a high-quality effluent under a variety of influent flow and organic-loading conditions. The sequencing batch reactor system eliminates the need for separate primary and secondary clarifications and a sludge recycle system because the sludge remains in the reactor at all times. Because of this constant concentration of mixed liquor within the system, there is a high tolerance for peak flows and shock loadings. The hydraulic retention time is easily controlled, thereby limiting the growth of filamentous bulking bacteria that reduce the settling characteristics of the sludge layer. In addition, sequencing batch reactor systems can typically achieve BOD removal efficiencies comparable to conventional activated sludge systems, ranging from approximately 85 to 95 percent.

Disadvantages

The main disadvantage of using a sequencing batch reactor system to treat contaminated groundwater would be its operation under low concentrations of influent organics. Other disadvantages include the need for automated valves, switches, level or flow sensors, and a programmable logic controller, which will require more operation and maintenance of the system. The increased level of sophistication generally equates to more items that can fail or will require maintenance.

Membrane Bioreactors

The membrane bioreactor (MBR) combines the suspended growth biological treatment with membrane filtration to provide an improved level of organic constituent removal. The membrane separator is used for solids removal and can replace the secondary clarification and effluent filtration steps. The bioreactor can operate at a much higher mixed liquor concentration because the need for sedimentation is eliminated. A membrane bioreactor can be configured with either internal or external membrane modules (refer to Figure 3-15). In a system with an internal membrane system, membrane modules are installed inside the suspended growth bioreactor. The membrane is subject to a vacuum to draw treated effluent (permeate) through the membrane while leaving solids in the reactor (retentate). Compressed air is introduced through a manifold at the base of the membrane to scour the membrane surface and oxygenate the water. A backflush process using a

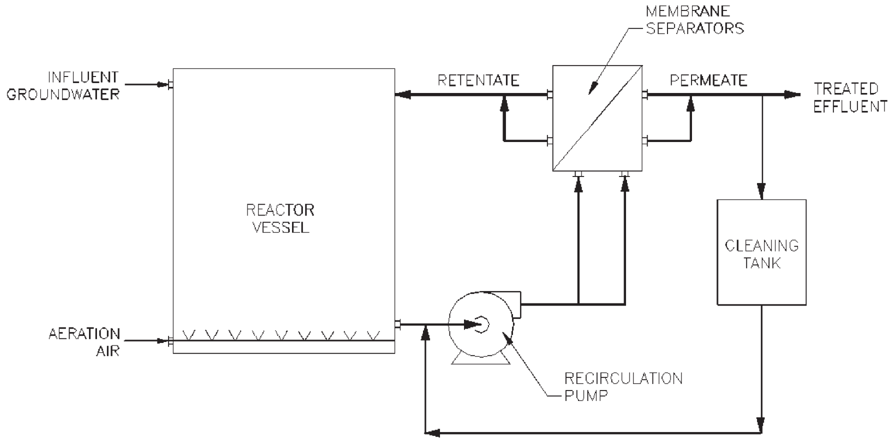


FIGURE 3-15. Example of a membrane bioreactor (MBR).

low concentration of chlorine can also be used to clean the membrane. An external membrane system consists of membrane modules outside the suspended growth bioreactor. Mixed liquor is withdrawn from the bioreactor and pumped at relatively high pressure through the membrane module; the retentate is returned to the bioreactor and the permeate is discharged as treated effluent. The membrane modules in the external membrane system operate in the same manner as the internal membrane system.

The mean cell residence time in a membrane reactor can range from fifteen to 365 days, depending on flow conditions. The longer solids retention time results in less sludge production than a conventional suspended growth system. The mixed liquor suspended solids concentration can range from 3,000 to 15,000 mg/L. Higher MLSS concentrations can be tolerated as the need for a good settling floc is no longer necessary.

Advantages

The advantages of using a membrane bioreactor are that it can handle increased volumetric loading rates, sludge production is significantly less than conventional systems, a smaller footprint is required, and the system can be easily expanded with additional modules. In addition, lower dissolved oxygen concentrations are necessary because of decreased BOD, and a high-quality effluent is produced with lower turbidity and total suspended solids.

Disadvantages

The disadvantages of using a membrane bioreactor are that the capital costs are higher, minimal information is available on membrane life, the cost for membrane replacement is potentially high, and membrane fouling will need to be controlled. Membrane fouling is a considerable concern, and several steps are necessary to control it. Coarse bubble aeration, backwashing the membrane every fifteen to thirty minutes (typically with a low concentration of chlorine), and back flushing the membrane with a citric acid solution three times per week, including two cycles of a rinse backflush, can be used to control fouling. The membrane modules can also be removed from the bioreactor and cleaned with a chemical bath. Despite regular cleaning, pressure drops across the membrane increase with time, and occasionally the modules will need to be removed for recovery cleaning.

Fixed-film Bioreactors

Fixed-film bioreactors are a type of ex situ biological treatment technology used to biologically degrade organic constituents in groundwater under aerobic, anoxic, or anaerobic conditions. In fixed-film systems, a large surface area inert medium is placed within the reactor vessel. The medium provides the following functions: a surface to support the attachment and growth of bacteria, forming a biofilm; and the means to facilitate the thorough mixing of contaminated water and air for oxygen transfer in aerobic systems and/or to distribute the water to come into contact with the biofilm.

Unlike suspended growth bioreactors that rely on methods to keep biomass within the vessel (e.g., clarifiers and sludge pumps, membrane separation), fixed-film bioreactors require a means to control excess biomass. In a well-designed and healthy system, the biomass inventory is self-regulating; excess biomass sloughs from the support medium and exits in the treated effluent. Some fixed-film bioreactor designs control biofilm simply by introducing oxygen (e.g., aeration) or though a mechanical shearing of the excess biomass from the medium.

There are two general classes of fixed-film bioreactors:

- *Trickling media:* Trickling media-style bioreactors are designed to distribute the wastewater stream in a thin film over the medium beds and biomass. The wastewater is sequentially distributed over a discrete portion of the medium, not the entire bed, as a means to control excess biomass (because the medium is not submerged, gravity promotes sloughing of the thickened biofilm). The organic constituents transfer into the biofilm; the bacteria degrade the organics; and the waste by-products (carbon dioxide and water) transfer back to the water film. Oxygen transfers from the atmosphere through the water film and to the biofilm. One important advantage of trickling media systems is that oxygen can be supplied at lower costs. The most common trickling media bioreactors are trickling filters and rotating biological contactors.
- *Submerged media:* This class of bioreactor employs a biomass support medium that is completely submerged within the reactor vessel. Excess biomass is typically controlled with aeration (e.g., coarse or fine bubble aeration provides a scouring action to promote sloughing of the thickened biofilm) or through the mechanical shearing of the biomass from the medium. The most common submerged media bioreactors are the submerged fixed-film bioreactor and the fluidized bed bioreactor.

Like suspended growth bioreactors, fixed-film bioreactors have been utilized for the treatment of hazardous organic chemicals in groundwater. However, because of the fundamental difference in biomass growth configurations, fixed-film bioreactors require different design approaches and are used for different applications. Similar to suspended growth bioreactors, microbial population and the degradation of organic contaminants are a function of the biomass inventory and mean cell residence time in fixed-film bioreactors. A decrease in biomass inventory or mean cell residence time often results in a decrease in treatment performance. In groundwater treatment applications, the concentration, the rate of degradation, and energy yield of certain organic chemicals are sometimes too low to support a suspended growth bioreactor and maintain a high mean cell residence time.[35] Because of the attached growth of biomass, the mean cell residence time of fixed-film bioreactors (particularly the submerged media class) is intrinsically higher than that of suspended growth bioreactors. This characteristic renders fixed-film systems more suitable for the treatment of low concentrations of organic compounds.

Trickling Filters

Figure 3-16 is a photograph of a trickling filter that employs a random plastic medium to support biomass growth. The contaminated water

FIGURE 3-16. Photo of a trickling filter with random plastic media. (Courtesy of Jaeger Environmental, www.jaegerenvironmental.com/)

FIGURE 3-17. Photo of a rotating distributor of trickling filter with random plastic media. (Courtesy of Jaeger Environmental, www.jaegerenvironmental.com/)

is pumped to the top of the reactor and distributed over the medium (typically employing a rotating distributor, see Figure 3-17). The water is broken up into thin films and trickles down through the medium. The contaminants transfer into the bacterial film and degrade. Oxygen transfers through the thin film of water and to the bacteria. Waste by-products (i.e., carbon dioxide) transfer out through the thin film of water to the atmosphere.

Several types of inert support medium can be used in a trickling filter. Originally, small (3- to 5-inch) rocks were used to support the bacterial population. However, rocks provided a relatively low biomass inventory in the system because of their low surface area per unit volume, as well as a low oxygen transfer capacity because of low void space. Plastic medium is more prevalent in trickling filters. The two main categories of plastic medium are random (dumped) packing and stacked packing. Random packing is similar to the type of plastic medium used in packed-tower air strippers (Figure 3-18). Stacked packing comes in large bricks (Figure 3-19) and is manufactured to deliver/transfer cross-flow or vertical flow patterns within the medium bed. Random packing is usually used as a replacement for rocks in existing trickling filters and small new systems. Stacked packing is usually applied to large systems. A third category of plastic medium that has been used over the last twenty years is the plastic strip-type medium (Figure 3-20).

FIGURE 3-18. Bio-rings random plastic media. (Courtesy of Jaeger Environmental, www.jaegerenvironmental.com/)

FIGURE 3-19. DURA-PAC cross-flow biomass support media. (Courtesy of Jaeger Environmental, www.jaegerenvironmental.com/)

Rotating Biological Contactor

Figure 3-21 is a schematic of a typical rotating biological contactor design. In this system, the water enters one end of the tank. The medium first rotates down into the water. The contaminants, once again, transfer to the bacteria. The medium then rotates up into the atmosphere; a thin film of water forms on the medium, and the oxygen transfers through the thin film of water and to the bacteria. Rotating biological contactors are probably the most energy-efficient oxygen transfer method for biological systems.

FIGURE 3-20. Sessil vertical plastic strip biomass support media. (Courtesy of Jaeger Environmental, www.jaegerenvironmental.com/)

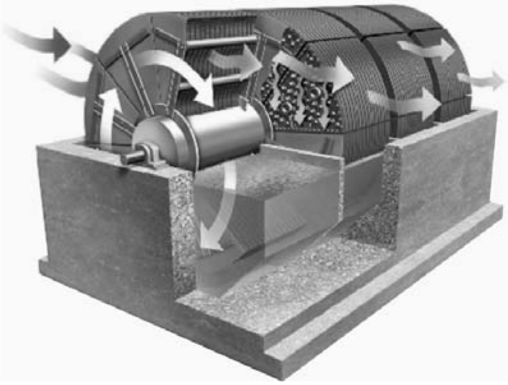


FIGURE 3-21. Schematic of an EnviroDisc rotating biological contactor (RBC). (Courtesy of Walker Process Equipment, www.walker-process.com/)

Advantages and Disadvantages

There are several technical disadvantages with trickling media fixed-film reactors. Trickling media fixed-film reactors are plug flow reactors, and contaminant concentration changes as a function of distance through the medium bed. The water comes in at one end, passes by the bacterial film, and exits the other end of the reactor. Thus, the influent end of the reactor sees the full strength concentration of the contaminant, unlike completely mixed reactors, in which influent concentration is diluted (the influent is immediately mixed with the contents of the tank). The influent concentration may be toxic, or pockets of high concentration material may be found as the groundwater is recovered from the heterogeneous geologic formation. The bacteria in the fixed-film reactor will be subjected to the full concentration. Recycling of the effluent water can be used to minimize this effect, but it also adds to the cost of operation.

Another problem with trickling media fixed-film reactors is that the removal efficiency of the influent contaminant is not as high as with an activated sludge system. Specific chemical removal is very important in groundwater treatment. General removal of organics will be important, depending on the final disposal of the water. The design engineer can expect 75 to 90 percent BOD removal and 85 to 95 percent removal of a specific organic. As discussed before, the lower the influent concentration, the less percent removal can be expected. A final problem with trickling media fixed-film reactors, particular in groundwater applications, is that they are prone to fouling from iron and hardness constituents.

Table 3-5 summarizes the advantages and disadvantages of trickling media fixed-film systems.

Submerged Fixed-film Bioreactors

Another category of biological treatment is a submerged media bioreactor, which is a combination of suspended growth and fixed-film reactor designs, referred to as submerged fixed-film reactors.

TABLE 3-5 Trickling Media Fixed-film Bioreactors

Advantages	Disadvantages
Low operator attention	Plug flow
Retention of low-yield and/or slow-growing bacterial populations	Limited operation at high influent concentrations
Low-cost oxygen transfer	Hard to adjust operation
Resistant to shock loads	Biofilm control is mainly provided by gravity sloughing, which provides very low mechanical shear
Relatively low sludge generation	Limited to groundwater or wastewater applications with low inorganic loading rates to prevent bridging and plugging of the media bed
	Prone to fouling/plugging with typical groundwater hardness constituents
	Filamentous biomass cannot be controlled without a strong chemical reagent program (e.g., chlorine, hydrogen peroxide)

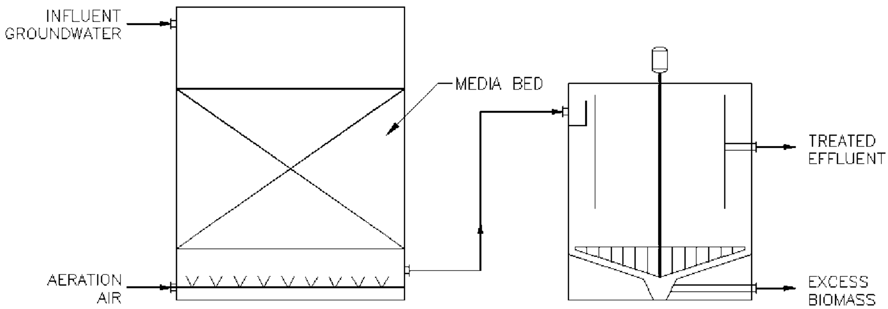


FIGURE 3-22. Simplified schematic of a submerged fixed-film bioreactor.

Figure 3-22 shows a simplified schematic of a submerged fixed-film unit.

In these units, the medium is placed in the reactor tank, and the water level is maintained above the height of the plastic medium. The bacteria grow on the plastic medium (or other solid support) as a biofilm (as in the rotating biological contactor and trickling filters described above). However, the water is in close contact with the film rather than passing through in thin films.

There are two main conditions in which the submerged fixed-film design can be used: (1) relatively high influent organic content (150 to 5,000 mg/L BOD), and (2) low organic content (less than 150 mg/L BOD). The first has been used for many years in wastewater treatment.[29] An example of a typical unit used for the treatment of groundwater is shown in Figure 3-23. In this mode, the reactor is designed for completely mixed operation and for high concentrations of organic influent. Influent groundwater is introduced in a downflow configuration. Air is released below the medium and travels up through the medium (refer to Figure 3-24 for a cross section of the aeration diffuser laterals; the example uses coarse bubble diffusers). With sufficient aeration, the biological reactor vessel is completely mixed.

The main advantages of the submerged fixed-film unit in this design mode are ease of operation and high-quality performance. Submerged fixed-film bioreactors can perform as well as an activated sludge unit, but it is not dependent on a clarifier for maintaining the bacteria in the reaction tank. This allows for a large variety of operating conditions and low operator attention. This reactor design combines the advantages of the suspended growth systems and the advantages of the fixed-film systems without the disadvantages of either. The main disadvantages of the submerged fixed-film design are the high cost of

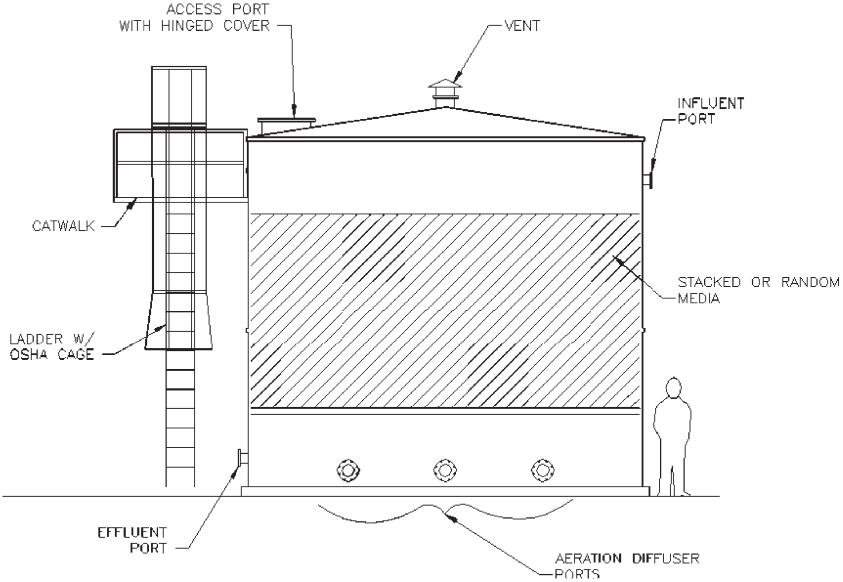


FIGURE 3-23. Schematic of a submerged fixed-film bioreactor (downflow configuration).

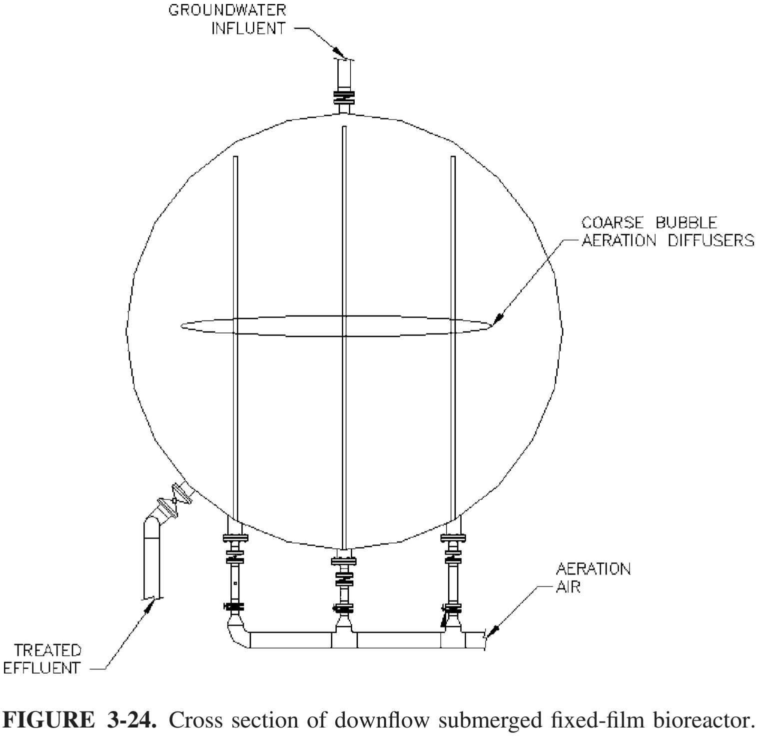


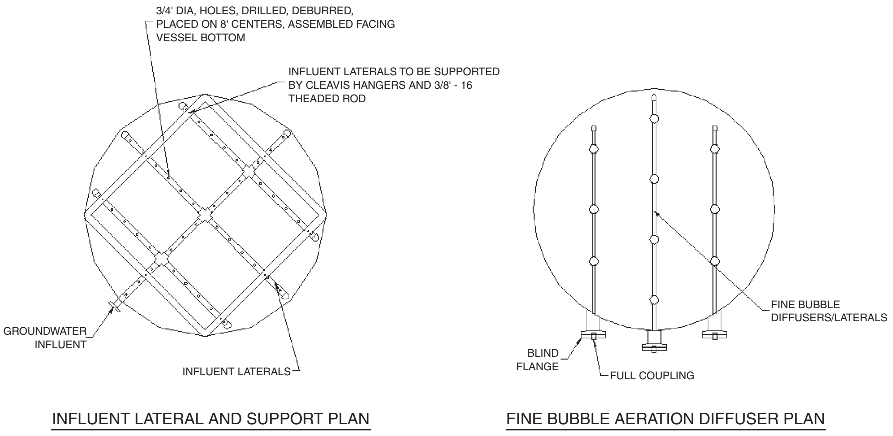
FIGURE 3-24. Cross section of downflow submerged fixed-film bioreactor.

oxygen transfer and lack of scalability. Because of the nature of the design, there is a natural height limitation to the tank, and, therefore, oxygen cannot be released at an optimum depth. In addition, diffused aeration is one of the more costly oxygen transfer methods. The second problem is the scaling of the unit. Suspended growth and fixed-film units cost relatively less as the systems get larger. Because the tank and the medium are both getting larger in direct relationship to the size of the system, the submerged fixed-film unit does not have large cost advantages for larger systems.

Neither of these disadvantages have a marked effect on groundwater applications. First, oxygen transfer is generally a small part of the total cost of a groundwater biological treatment system (many groundwater applications have a fairly low concentration of organics, less than 150 mg/L BOD). Second, most groundwater treatment systems are relatively small, and the cost advantage of large-scale systems does not apply.

A second mode in which the submerged fixed-film units can be applied to groundwater is a low-concentration design. Submerged fixed-film bioreactors can be designed to treat influent concentrations as low as 1 to 20 mg/L. This is very important for groundwater applications because relatively low concentrations of organics (less than 150 mg/L BOD) are commonly found in groundwater.

Figure 3-25 depicts plan view cross sections of a low-concentration design of a submerged fixed-film unit. The basic design is the same as the original submerged fixed-film design except that an influent distribution lateral system is used to more evenly distribute groundwater



INFLUENT LATERAL AND SUPPORT PLAN

FINE BUBBLE AERATION DIFFUSER PLAN

FIGURE 3-25. Cross section of a low organic loading submerged fixed-film bioreactor.

to the top of the vessel. The plastic medium is submerged below the water level in the reactor tank. The low-concentration reactor uses small amounts of air (fine bubble diffusers are used) and a plug-flow pattern. The water enters the top of the tank and is distributed across the medium. The water flows down through the medium and exits the bottom through a collection system. The air is released below the medium. Very small amounts of air are used because of the low requirement for oxygen demand in a low-concentration reactor and the need to maintain a non-mixed state in the reactor.

Even under these conditions, the low concentration of inflow organics is not sufficient to maintain an adequate biomass inventory within the reactor. Normally, influent concentrations of less than 50 mg/L will result in bacteria decay faster than new bacteria can grow to replace the old bacteria. Therefore, the low-concentration reactor must operate in a decay mode, not the normal growth mode of biological treatment systems. In this decay mode, bacteria are grown on the fixed film from a synthetic feed source. When the bacteria have established a full population, the synthetic feed is removed, and the low-concentration influent is conveyed through the system. Under these conditions, the bacteria slowly decay. With the proper design and operation, the decay period can last between six months and one year before regrowth is required.

The low-concentration reactors have been out of the laboratory and pilot-plant stage for many years. The authors have personally designed over 50 full-scale units as part of a groundwater remediation. Compounds that have been treated in this reactor design have ranged from acetone and methyl ethyl ketone to benzene and chlorobenzene. These reactors have also been used successfully to treat tetrahydrofuran and *t*-butanol.

The growth of some specialized bacteria cultures, which are capable of degrading certain organic chemicals, are encouraged under biofilm growth conditions. Because of the more intense competition for substrates in suspended growth bioreactors, the activities of fast-growing bacterial populations are often favored, whereas those of slow-growing bacteria are suppressed. The slow-growing bacteria are usually capable of degrading recalcitrant organic chemicals, which are mostly low-specific-growth-rate substrates (e.g., <0.1 hour^{-1} for some aromatic organic compounds compared to 0.3 hour^{-1} for domestic wastewater), found in contaminated groundwater.[35] Submerged fixed-film bioreactors are excellent for use in a polishing step to remove recalcitrant organics following treatment with a suspended growth bioreactor that facilitates bulk removal of the easier to degrade organics.

Advantages

The main advantages of the submerged fixed-film unit in the complete-mix, high organic loading design mode are ease of operation and high-quality performance. Submerged fixed film can perform as well as an activated sludge unit, but it is not dependent on a clarifier for maintaining the biomass inventory. This allows for a large variety of operating conditions and low operator attention. This reactor design combines the advantages of both the suspended growth systems and the fixed-film systems with fewer of the disadvantages of either.

Disadvantages

The main disadvantages of the submerged fixed-film design are the high cost of oxygen transfer and lack of scalability. Because of the nature of the design, there is a natural height limitation to the tank, and therefore, oxygen cannot be released at an optimum depth. In addition, diffused aeration is one of the more costly oxygen transfer methods. The second problem is the scaling of the unit. Suspended growth and fixed-film units cost relatively less as the systems get larger. Because the tank and the medium are both getting larger in direct relationship to the size of the system, the submerged fixed-film unit does not have large cost advantages for larger systems. Like the fixed-film technologies, plugging of the medium can be an issue if the groundwater contains high iron and/or hardness constituent concentrations. Also, filamentous biomass can cause plugging of the medium.

Table 3-6 summarizes the advantages and disadvantages of submerged fixed-film bioreactors.

Design

Design of submerged fixed-film bioreactors is often based on the loading rate in pounds of target contaminant (e.g., BOD, nitrate as nitrogen [NO_3-N] per unit volume of the growth media within the vessel (cubic feet). Table 3-7 summarizes typical process loading ranges for conventional submerged fixed-film bioreactors. Bench-scale treatability testing and pilot-scale testing are recommended prior to designing a treatment system employing submerged fixed-film bioreactors.

Fluidized Bed Bioreactor

The fluidized bed bioreactor (FBR) is a type of submerged media bioreactor that is operated in an upflow condition where the superficial velocity of the process water introduced to the vessel is high enough to expand the media bed (typically sand or granular activated

TABLE 3-6 Submerged Fixed-film Bioreactors

Advantages	Disadvantages
Low operator attention	Relatively high cost of oxygen transfer
Retention of low-yield and/or slow-growing bacterial populations	Limited to relatively small units due to lack of scalability
Resistant to shock loads	Biofilm control is provided by the scouring action of the aeration system, which provides relatively low mechanical shear
Can be operated at high organic loading in complete mixed mode as wells a low organic loading in plug flow mode	Limited to groundwater or wastewater applications with low inorganic loading rates to prevent bridging and plugging of the media bed
Can be operated under aerobic conditions, anoxic conditions (e.g., chlorinated organics, nitrates, perchlorate, hexavalent chromium), or anaerobic conditions	Filamentous biomass cannot be controlled without a strong chemical reagent program (e.g., chlorine, hydrogen peroxide)
Can be employed as a polishing step to remove harder to degrade organics under low organic loading conditions	
Can be operated as an extended aeration step downstream of an activated sludge system for ammonia control	
Relatively low solids generation	

carbon) to more than 50 percent of its static packed-bed form.[37] The expansion is a result of drag force caused by the fluid flow through the support media against gravity. The superficial velocity for typical FBR designs (there are variations in the way in which influent is distributed throughout the cross-sectional area of the vessel between FBR manufacturers) ranges between 10 and 15 gpm per square ft of the vessel cross-sectional area (gpm/ft^2).

Throughout the course of the FBR's operation, the mass, diameter, and density of the media changes as a result of biomass growth (e.g., media particles with thicker biofilm migrate upward through the bed since the increased diameter imparts more buoyancy) and the bed continues to expand. Without a means to control the biofilm, the bed expansion will continue until media is wasted from the vessel with the treated effluent. Bed expansion can be controlled by the removal/cleaning/reintroduction of media or in-vessel cleaning of biomass growth using a mechanical shearing device, which is commonly included in skid-mounted FBR units.[35] Figure 3-26 presents a simplified schematic of an FBR.

Advantages

Due to the large surface area of the support media, FBRs are excellent choices for treatment of low concentrations of specific constituents.

TABLE 3-7 Design Criteria for Submerged Fixed-film Bioreactors

Loading Range	Operational Category	Removal	Loading
High rate (requires pretreatment to remove solids and scale-forming constituents such as iron)	Aerobic complete mix	85–95% BOD	60–90 lb BOD/1,000 cu ft media/day
Typical groundwater (may require pretreatment to remove solids and scale-forming constituents such as iron)	Aerobic complete mix	85–99% BOD	30–60 lb BOD/1,000 cu ft media/day
Low rate (may require a supplemental carbon source)	Aerobic plug flow	85–99% BOD	10 lb BOD/1,000 cu ft media/day
Nitrification (may require a supplemental carbon source, requires oxygen at a 4.6 pounds per pound of ammonia nitrogen [NH_4-N])	Aerobic complete mix	85–95% NH_4-N	5–30 lb BOD/1,000 cu ft media/day
Denitrification (requires a supplemental carbon source)	Anoxic plug flow	85–95% NO_3-N	5–10 lb NO_3-N/1,000 cu ft media/day
Denitrification (requires a supplemental carbon source)	Complete Mix, Two Reactors in Series (Lead/Lag)	85–95% NO_3-N	60–120 lb NO_3-N/1,000 cu ft media/day
Anoxic treatment of chlorinated compounds, perchlorate, chromium, etc. (requires a supplemental carbon source)	Anoxic plug flow	95–99% target contaminant	10–60 lb target contaminant/1,000 cu ft media/day

Disadvantages

Inherent to their design, FBRs are limited to low-concentration applications. If the influent organic concentrations exceed 120 milligrams per liter (mg/L) of total organic carbon (TOC), biomass develops too rapidly for the biofilm control mechanisms, and wastage of the media inventory occurs.

Oxygen transfer is expensive since conventional aeration systems, such as coarse bubble aeration and fine bubble aeration, are not possible due to the plug flow nature of the design. In most FBR designs, oxygen is transferred to a combined influent and recycle stream using a bubble contactor fed with oxygen. Depending on the size of the FBR system (carbon loading and oxygen demand), the oxygen can be supplied via pressurized tanks or through the use of a pressure swing adsorption (PSA) system. A PSA is essentially an air compressor that employs zeolites to adsorb nitrogen.

Table 3-8 summarizes the advantages and disadvantages of FBR systems.

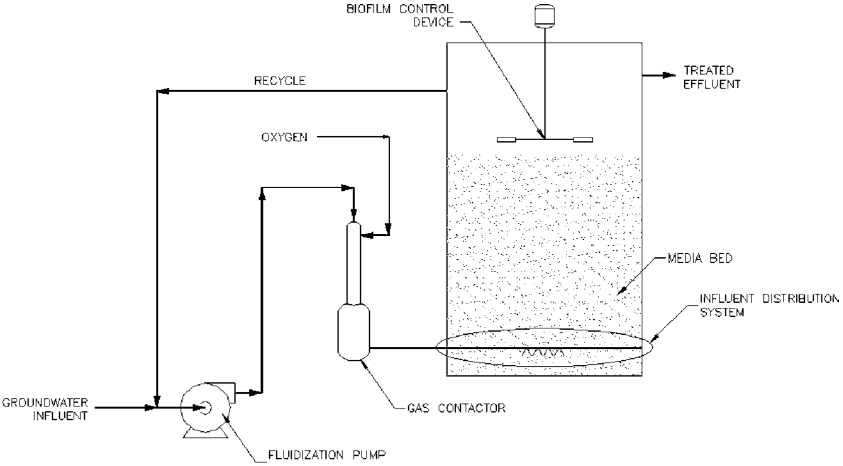


FIGURE 3-26. Schematic of a fluidized bed Bioreactor.

TABLE 3-8 Fluidized Bed Bioreactors

Advantages	Disadvantages
Low to moderate operator attention	High cost of oxygen transfer
Retention of low-yield and/or slow-growing bacterial populations	Limited to relatively small units due to lack of scalability
Can be operated under aerobic or anoxic conditions (e.g., chlorinated organics, perchlorate, hexavalent chromium)	Biofilm control is provided by slow mixing devices, small air-lift devices to lift carbon from the bed and scour with air bubbles, and media pumpout/return systems, to promote mechanical shear
Can be employed as a polishing step to remove harder to degrade organics	Limited to groundwater or wastewater applications with low inorganic loading rates to prevent bridging and plugging of the media bed
Low solids generation	Filamentous biomass cannot be controlled without a strong chemical reagent program (e.g., chlorine, hydrogen peroxide) or a high mechanical shear system
	Biomass support media wastage will occur, so media replenishment is an ongoing operating expense

Design

The most important design parameter for implementation of FBR technology is the hydraulic retention time (HRT). For FBR systems, the HRT is determined as follows:

$$\text{HRT} = \text{gpm} \div \text{media volume}$$

The following is a summary of design parameters for FBRs. Bench-scale treatability testing and pilot-scale testing are recommended prior to designing a treatment system employing FBR technology.

Maximum influent TOC: 120 mg/L
HRT: 10 to 90 minutes
Fluidization flow rate: 10 to 15 gpm/ft^2
If TOC $<$ 40 mg/L, recycle may not be needed
If TOC $\geq$ 40 mg/L, recycle required
Loading: $\leq$ 60 lb TOC/1,000 cu ft media/day

Sedimentation/Clarification

With the exception of SBRs and MBRs, most bioreactor technologies employ gravity sedimentation to separate solids from treated effluent. In the case of suspended growth reactors, the suspended biomass settles and thickens via gravity and is then conveyed back into the reactor vessels. Thus, the sedimentation operations are an integral component of the bioreactor. Since fixed-film reactors maintain the biomass inventory on some type of media, downstream sedimentation operations are employed as a treatment process for removal of suspended solids, either prior to additional treatment in a downstream process or prior to final discharge.

Sedimentation refers to the gravitational settling of solid particles within a bulk liquid. Four types of settling have been identified in the sedimentation process where water is the bulk liquid and the solid particles are denser than water:[31,34]

- *Type I—discrete particle settling*: Discrete settling refers to the settling of individual particles through a quiescent liquid. In type I settling, there is no chemical or physical interaction between particles (e.g., gravity and frictional drag are the only forces acting on the particles).
- *Type II—flocculent settling*: Flocculent settling refers to the agglomeration of discrete particles into larger particles during the sedimentation process. In type II settling, the agglomeration is facilitated by changing the settling characteristics of the particles, most typically using a coagulant aid such as lime or ferric chloride and a high molecular weight organic polymer as a flocculant aid. The settling velocity of flocculating particles changes with time as the effective diameter of the particles increases.

- *Type III—hindered (zone) settling*: Hindered or zone settling refers to a high concentration of particles in which some of the particles are in contact with other particles. In type III settling, the settling of individual particles is hindered by the interaction of the neighboring particles within the matrix. As a result, the bulk of the particles settle as a zone, maintaining the same relative position with respect to each other (e.g., sludge blanket). The solids flux consists of the gravitational settling of the sludge and the movement of the sludge withdrawal from the bottom of the clarifier (commonly referred to as clarifier *underflow*).
- Type IV—*compression settling*: Compression settling refers to the settling of the particles after they have come into complete contact with one another in a matrix. Type IV settling is characterized by a rearrangement of the particles within the matrix or by a compression of the particles and matrix.

Clarifiers

Clarifiers should be designed in conjunction with the needs of the bioreactor: (1) to separate biomass from treated effluent and return it to the reactor vessel to maintain the optimal biomass inventory, or (2) to separate suspended biomass from a fixed-film bioreactor to remove solids prior to conveyance to additional treatment operations or final discharge. The following discussion focuses primarily on the first type of clarifier design for use in a suspended growth bioreactor system.

A healthy biomass will perform efficiently to remove contaminants and will settle better. Generally, in the clarifier stage, the solids in the bioreactor effluent stream settle out by the types of sedimentation described above forming a sludge blanket. Sludge is removed as an underflow and either wasted (waste activated sludge [WAS]) or returned (return activated sludge [RAS]) to the bioreactor to maintain the health of the biomass. A clear water zone forms on top and overflows to the next stage in the treatment system. There are many components to consider when designing the clarifiers.

Solids Removal

As discussed above, type III hindered or zone settling is the governing type of settling for activated sludge clarifiers. In type III settling, the solids settle in a blanket, reducing the settling velocity. This type of settling can be visualized by thinking of a cross section of the clarifier. Near the surface of the clarifier is essentially clear water. Below the liquid surface, type I and type II settling occurs, where particles are settling by gravity: heavier discrete particles drop at a constant velocity while the flocculating particle's velocity changes over time as the particles increase in size (since a healthy biomass inventory consists predominantly of floc forming bacteria). The type I and II settling zones exhibit increasing turbidity as the depth below the liquid surface increases. At the type III settling zone, a distinct liquid/slurry interface is visible. This interface is commonly referred to as the top of the sludge blanket. In the type III settling zone, the solids concentration is elevated, but the gravity settling rate is slowed significantly (thus the zone is referred to as *hindered*). As the depth below the clarifier surface increases, the slurry concentration increases until the blanket is in the type IV compression settling zone, where the weight of the blanket actually compresses the slurry, essentially squeezing out water, resulting in a thicker slurry. Typically, clarifiers are equipped with a sludge collector mechanism (sludge rake). The sludge rake facilitates additional dewatering/thickening by scraping the sludge and turning the blanket over. Figure 3-27 is a schematic of the log of

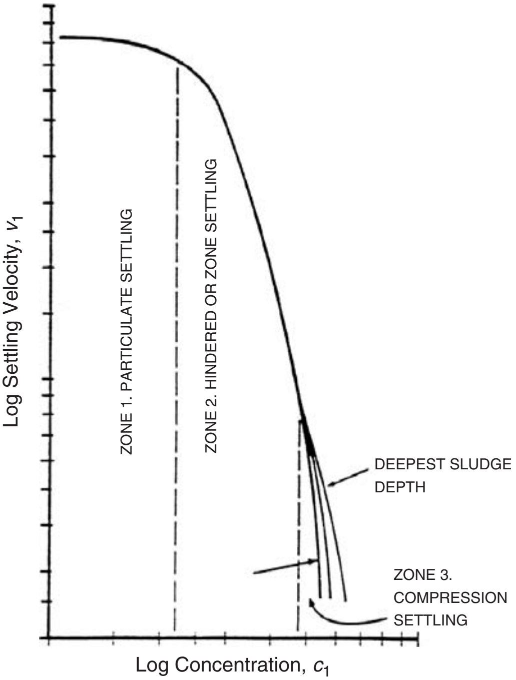


FIGURE 3-27. Illustration of clarifier settling zones. (Courtesy of Walker Process Equipment, www.walker-process.com/)

particle/blanket settling velocity versus the log of slurry concentration depicts the concepts of the various settling zones.

The schematic helps to illustrate why maintenance of the optimal sludge blanket is crucial for efficient solids removal. For example, if the RAS/WAS pumps were shut down for an extended period of time; the depth of the compressed sludge would increase. However, the other settling zones do not get smaller to compensate. Rather, the settling zones shift upward toward the liquid surface (e.g., the effective settling depth of the clarifier is reduced). The further the zones shift closer to the surface of the clarifier, the less effective the clarifier becomes at removing solids.

For activated sludge clarifier design, a common approach is used to determine the area required for type III settling, known as *solids-flux* analysis. Since hindered settling occurs in a continuous mat or blanket throughout the cross-sectional area, flux is the design parameter used in the analysis. Flux is defined as the rate at which mass will pass through a unit area, in this case pounds per day per square foot (lb/day-ft^2). In addition to gravity hindered settling described above, the flux of solids in type II settling is influenced by the bulk transport of fluid from the bottom of the clarifier (e.g., underflow). The underflow refers to the pumping rate of the RAS/WAS Pumps. Figure 3-28 illustrates the concepts behind the solids-flux analysis method of design.

As shown in the figure, the higher the concentration of solids in the underflow (e.g., if thickening is an objective of the clarifier), the lower the solids flux the clarifier is capable of. In other words, more settling area is required to achieve the desired solids removal.

This demonstrates that the underflow pumping rate determines the solids concentration. With a given inflow rate, a given inflow solids concentration, and a given clarifier settling area, the parameter that

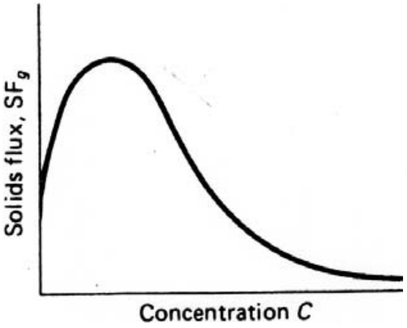


FIGURE 3-28. Solids flux and solids concentration graph.

controls the underflow concentration is the underflow pumping rate. The best approach an operator can employ to check the optimal pumping rate (whether it be RAS or WAS) is to determine the quantity of solids entering the clarifier (MLSS from the aeration basins), assume 100 percent capture of the solids, then calculate the pumping rate to yield the target underflow solids concentration. For example,

Given

MLSS concentration: 3,000 mg/L
Target solids in underflow: 3 percent solids
Inflow to clarifier: 250 gpm
Solids load to clarifier:
250 gal/min × 1440 min/day × 8.34 lb/gal × 3,000 ppm MLSS ÷ 1,000,000 gal/MG = 9,000 lb/day solids
Required underflow pumping rate:
24,000 lb/day solids ÷ 8.34 lb/gal ÷ 0.03 ÷ 1440 min/day = 25 gpm

Most fixed-film bioreactors produce a relatively low solids content in the treated effluent (typical range of 25 to 250 mg/L of TSS). Clarifier designs for fixed-film bioreactors, therefore, are most often designed based on hydraulic loading (gallons per day per square feet of clarifier [gal/day-ft^2]) since the solids loading is too low to design based on solids flux. Most clarifiers employ a weir as a means to facilitate overflow of clarified effluent. The weir loading rate is another important design criteria (gallons per day per linear feet of weir [gal/day-ft], if the influent flow rate to the clarifier is much higher than its design, turbulence could result within the clarifier, disturbing the settled sludge blanket and resulting in poor solids removal. Table 3-9 provides typical design criteria for clarifiers used with suspended growth and fixed-film bioreactor systems employed in groundwater treatment applications.

It should be noted that inclined plate clarifier designs are not recommended for use with suspended growth or fixed-film reactors. It is the authors' experience that biomass will bridge the gaps between the clarifier's plates and incorporate the solids into the biomass network, and plug the plates relatively quickly.

TABLE 3-9 Clarifier Design Criteria

Solids loading	5–20 lbs/day-ft^2
Maximum hydraulic loading	350–1,000 gal/day-ft^2
Maximum weir loading rate	10,000 gal/day-ft
Sidewater depth	$\geq$10 ft

Solids Handling

As the sludge is wasted from the clarifiers it will be stored until it is disposed of. Many options are available for disposal, depending on the characteristics of the sludge and the regulations in the area. Options to consider include land application, landfilling, or even distribution and marketing. Until the sludge is actually disposed of, the holding tank should be mixed continuously and aerated periodically to keep the sludge from going septic and to reduce odor.

Depending on the method of disposal, dewatering may be an economical option to reduce water weight. Many options are available to dewater sludge, depending on the characteristics and the desired outcome. These options include centrifuges, belt filter press, pressure filter press, drying beds, and reed beds.

For wastewater treatment systems, sludge handling might include conditioning, stabilization, and a disinfection process. However, due to the characteristics of the sludge generated from the biological treatment of groundwater (e.g., large percentage of inorganic solids and absence of human or animal waste stream), these processes are typically not necessary in groundwater applications.

TYPICAL ANCILLARY PROCESSES

Ancillary processes are those that are outside of the standard process flow of a biological treatment technology for the treatment of groundwater. However, ancillary processes are critical to the process operations. Examples of ancillary processes include supplying oxygen and nutrients to the bioreactor; dewatering operations, including supply of compressed air and polymer for proper operation of the dewatering systems; and supplying chemicals used to control the physical characteristics of the process fluid, including acid/base addition for pH control, defoamer addition to reduce foaming issues. More detailed descriptions of select ancillary processes are presented below.

Aeration Equipment

There are a variety of reasons why aeration is important to a treatment system. Aeration can be used to achieve complete mixing within a tank, introduce oxygen into a treatment system to supply oxygen for biological activity, and supply oxygen for physical/chemical treatment. One or more of these factors will need to be taken into consideration when designing the system. Specification of the size and type of the aeration equipment will be based on the greatest aeration/oxygen need for the given conditions.

Numerous methods are employed to transfer oxygen into biological reactors, including surface mixers/agitators, step aeration, coarse bubble diffused aeration, fine bubble diffused aeration, jet mix aeration, and bubble contactors. However, for most reactor designs employed for groundwater treatment (FBR systems are a notable exception since they typically employ gas contact columns, as previously discussed), diffused aeration methods predominate because they are low capital cost, easy to implement, and simple to operate. Diffused aeration performance increases with submergence depth (e.g., the longer the air bubbles are in contact with the liquid, the better the mass transfer) to a practical limit of 20 feet or so.

In the preliminary design of a coarse or fine bubble diffuser system, the following parameters are needed: (1) the actual oxygen requirement (AOR) needed by the biomass for treatment (in pounds of oxygen per day [lb/day]), and (2) the minimum amount of oxygen, at standard conditions, to be provided by the diffuser system referred to as the standard oxygen requirement (SOR) in lb/day. A blower is employed to provide air at a sufficient pressure to overcome the head of the water above the diffusers. For groundwater applications, the AOR is equivalent to the BOD loading to the system multiplied by a safety factor to ensure that oxygen is not limiting. The authors' have successfully employed and recommend a safety factor of 25% (e.g., AOR = BOD × 1.25). Table 3-10 provides a summary of design data, including the standard oxygen transfer efficiency (SOTE), for coarse and fine bubble diffusers.

The design data provided should be used for preliminary estimates only. Diffuser manufacturers will provide the diffuser arrangement and aeration air requirements based on their experimental data that

TABLE 3-10 Diffused Aeration Design Data

Design Parameter	Coarse Bubble Diffuser	Fine Bubble Diffuser
Minimum aeration required for complete mixing	30 scfm/1,000 ft^3 of reactor volume	0.12 scfm/ft^2 of reactor area
SOTE	0.5–0.75%/ft of submergence	1.5–2.0%/ft of submergence
SOR	[AOR ÷ 0.50] lb/day	[SOR = AOR ÷ 0.33] lb/day
Aeration air required	[SOR ÷ SOTE ÷ 0.0173 ÷ 1440] scfm	[SOR ÷ SOTE ÷ 0.0173 ÷ 1440] scfm
Blower delivery pressure	[Submergence depth × 1.15 ÷ 2.31] psig	[Submergence depth × 1.15 ÷ 2.31] psig

incorporates temperature, elevation data, fouling components in the wastewater, etc.

High organic loading to the bioreactor and/or inorganic oxygen demand may require higher flow rates of air than required for mixing alone. The two most common types of blowers employed with air diffuser systems are multistage centrifugal blowers and rotary lobe positive displacement blowers. Centrifugal blower systems are typically more expensive than positive displacement blowers, but require less maintenance. Adjustments of aeration air flow rate from centrifugal blowers can be facilitated by a control valve located on the inlet of the blower. Positive displacement blowers can cost less but require frequent routine maintenance (adding oil and or grease to the bearings, replacement of belts, etc.). Adjustments of aeration air flow rate from positive displacement blowers can be facilitated by variable speed drives.

Dewatering Equipment

Dewatering equipment (filter presses, belt filter presses) are used to remove water from a thickened sludge to reduce costs associated with transportation and/or disposal costs. The filtered water (filtrate) is often collected and reused within the treatment train or recirculated back to the headworks of the treatment train for processing. Typical ranges for process solids entering dewatering operations can range from 2 to 10 percent, and effluent concentrations can be as high as 20 to 30 percent, based on the characteristics and preparation of the sludge (e.g., coagulant and/or polymer addition). Industry standard equipment used for sludge dewatering is presented below.

Belt Filter Press

One type of dewatering is performed by a belt filter press. The following describes the basic operation of a belt filter press.

- Flocculated sludge is evenly distributed onto the porous belt, which moves through a series of plows and/or dams. The free liquid is removed by gravity drainage.
- As the cake proceeds forward, the bottom belt and top belt gradually compress. This forms a wedge that applies low nonshear pressure.
- The sandwiched sludge moves into the medium-and high-pressure zones through a combination of rollers that decrease in size.

- After the last pressure roller as the belts separate, the cake is scraped off the belts, and each belt continues moving through the belt wash stations and back to the beginning of the process.

Filter Press (Plate and Frame)

A filter press is similar to a belt filter press in that it uses pressure to remove water from the solids. A plate and frame filter press consists of a series of chambers containing square or rectangular filter plates supported in a frame. Once the filter chambers are loaded with slurry, the plates are forced together with hydraulic rams that generate pressures typically in the region of 100 pounds per square inch. Each plate is covered by a material or membrane that acts as the initial filter when the press is in operation. As the solid filter cake builds up, the cake adds to the removal of fine particles. At the end of the compression, the solid filter cake is removed.

Chemical Feeding System

Chemical feeding systems are vital to the smooth operation of a biological groundwater treatment system. Feed systems are often required to deliver chemical at concentrations in the low parts per million (ppm) ranges, resulting in flow rates ranging in the low gallons per hour range or low gallons per day range, as opposed to the gallon per minute ranges of the treatment system it is feeding. Therefore, it is important for the design engineer to carefully consider the chemical feeding systems during design activities. Chemical feeding systems are typically outfitted with two chemical metering pumps to facilitate undisrupted flow of the chemicals to the treatment system.

Nutrients

Two key nutrients are nitrogen and phosphorous, and their availability is important to biological treatment systems as it affects how well organisms metabolize the carbon substrate as well as how well the generated biomass will settle. Typically, maintaining a residual ammonia of 1.0 mg/L (as nitrogen) and a residual orthophosphate of 0.1 mg/L (as phosphorus) is sufficient to ensure that the biological treatment process is not nutrient limited. The metering rate of the nutrients to the treatment system is determined by the uptake of the nutrients within the biological reactors by the microorganisms. To facilitate proper metering of the nutrients, the nutrient feed line is typically fitted with a calibration cylinder that, when used in conjunction with a stopwatch, allows for the measurement of the nutrient flow rate from the pump to the treatment system. For most groundwater applications, the form of nitrogen and phosphorous is provided with urea and phosphoric acid.

pH

A pH level of 6.5 to 8.5 is typical for biological treatment of groundwater. This range promotes optimum cell growth for the microorganisms. Care should be taken that the pH does not drop below 6.5 as this can promote or exacerbate the formation of filamentous biomass (typically fungi).

Since CO_2 is a by-product of aerobic metabolism, the biological treatment process will result in an elevation or depression in pH, depending on the method used for transferring oxygen. For reactors that employ diffused aeration, the pH will tend to rise because CO_2 is stripped by the aeration. FBRs, for instance, dissolve oxygen into solution using a gas contacting column; thus the CO_2 remains in solution and forms carbonic acid which depresses the pH. Also, if nitrification is occurring within the bioreactor, 7.4 mg/L of alkalinity is consumed for every mg/L of NH_4-N oxidized, resulting in reduced pH.

With many groundwater sources, however, pH adjustment may not be necessary since the groundwater is buffered with alkalinity. The buffering capacity of groundwater is its capacity to resist changes in pH. It results from the presence of weak acids and their salts or weak bases and their salts. It can be a challenge to adjust pH within a narrow range for water with a low buffering capacity because addition of small quantities of acid or base can result in large changes in pH. It is much more difficult to adjust the pH of water with a very high buffering capacity, either at alkaline conditions with pH greater than approximately 9.6 or acid conditions with pH less than approximately 4.3. It takes a large amount of acid to neutralize the buffering capacity (alkalinity) to ~9.6 from a higher starting pH, but typically much less acid to lower pH beyond this buffered end point. Similarly, it takes a large amount of base to neutralize the buffering capacity (acidity) to ~4.3 from a lower starting pH, but typically much less base to raise pH beyond this buffered endpoint.

Alkalinity is a measure of the capacity of the groundwater or waste water to neutralize a strong acid (e.g., sulfuric acid [H_2SO_4]) to a target pH. Alkalinity is expressed as an equivalent amount (in milligrams per liter [mg/L]) of calcium carbonate ($CaCO_3$). In groundwater and surface waters, this capacity is attributable to bases such as bicarbonate (HCO_3^{2-}), carbonate (CO_3^{2-}), and hydroxide (OH^-), as well as to species present in small concentrations (e.g., silicates, borates, ammonia, phosphates, and organic bases).[32]

Acidity is a measure of the capacity of the groundwater or waste water to neutralize a strong base (e.g., sodium hydroxide [NaOH]) to a target pH. Acidity is also expressed in mg/L of $CaCO_3$. Strong mineral acids like H_2SO_4 and weak acids like carbonic or acetic acids, as well as metal salts such as ferrous or aluminum sulfate, contribute to the acidity of the water.[32]

Figure 3-29 presents a graphical depiction of alkalinity and acidity across the full range of pH.[30]

To properly design a pH adjustment system, it is important to properly characterize the water. What is the pH? What is the buffering capacity? Will the process stream have a stable or variable pH/buffering capacity? Characterization of the following factors is critical:

- Flow rate of influent process water
- Acidity for acidic waters
- Total alkalinity, bicarbonate alkalinity, carbonate alkalinity, and hydroxide alkalinity for water with pH greater than 4

Once the above information is known, a neutralizing agent can be selected. Table 3-11 presents a summary of common bases and acids employed for pH control in groundwater treatment applications.

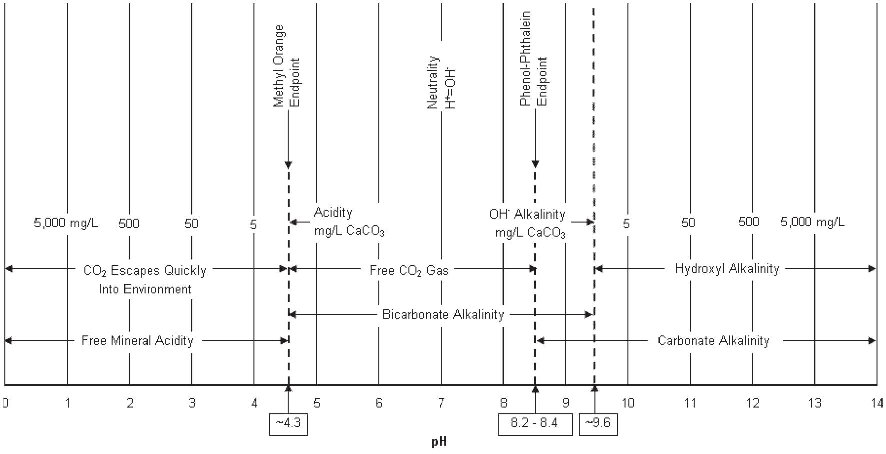


FIGURE 3-29. A graph showing alkalinity and acidity across the full range of pH.

TABLE 3-11 Neutralization Capability of Common Alkaline and Acid Reagents[33]

Chemical	Formula	Equivalent Weight	To neutralize 1.0 mg/L acidity or alkalinity (expressed as $CaCO_3$) requires n mg/L
Calcium carbonate	$CaCO_3$	50	1.000
Sodium hydroxide	NaOH	40	0.799
Sodium carbonate	Na_2CO_3	53	1.059
Sodium bicarbonate	$NaHCO_3$	84	1.680
Sulfuric acid	H_2SO_4	49	0.980
Hydrochloric acid	HCl	36	0.720
Nitric acid	HNO_3	62	1.260
Carbonic acid	H_2CO_3	31	0.620

Source: WEF Manual of Practice FD-3: Pretreatment of Industrial Wastes.

Defoamers

Heavy foaming within a biological treatment system can often lead to various processing problems. These problems range from inaccurate readings from control and measuring equipment, such as temperature, level, pH, and dissolved oxygen, to products hanging in the foam. Additionally, the presence of foaming can give a bad image of the way a process is operated in the eyes of a client. The presence of foam in discharged effluent can cause complaints from local people and authorities even if the foam is harmless to people and the environment. As a result, it is important to control and, to the extent possible, prevent the formation of foam. Providing for delivery of antifoam is a recommended practice. It has been the author's experience that addition of a defoamer at 1 to 10 mg/L based on influent flow rate is adequate to control most foaming occurrences.

It has also been the author's experience that some groundwaters contain surfactants from in situ biological activity. When the natural surfactants are mixed, particularly in aeration systems, significant foaming can occur (generally a white, billowing foam). Simple jar testing can be employed to determine whether the design should incorporate antifoaming systems regardless of the health and efficacy of the biological treatment system.

During the startup phase of the treatment system implementation, significant foaming can be expected from the biological treatment processes employing suspended growth and submerged fixed-film reactor designs. During the initial growth phase as the biomass inventory is ramping up, surfactants are released that cause this foaming. The foam is typically a white, voluminous, billowing foam. This same phenomenon can occur in suspended growth reactor systems under the following conditions:

- MCRT is too short (e.g., young sludge)
- Low pH, dissolved oxygen, orthophosphate or food-to-mass ratio is contributing to proliferation of filamentous biomass
- Cold weather or toxicant inhibiting microorganisms

Another type of foam can develop in suspended growth bioreactor systems: a thick, viscous, dark brown foam that looks like chocolate mousse, caused by the proliferation of the filamentous bacteria *Nocardia*. This type of foam is observed when the MCRT is too long (e.g., old sludge).

SUMMARY

Biological treatment is an important technology for remediation of contaminated sites. This chapter has provided a detailed review of the bacteria, their biochemical reactions, and the reactors in which they grow.

The most important points to remember about biological treatment is that it is a natural process and that it is probably already occurring at the site. The main objective of biological remediation designs is to remove the limiting factors in the growth of the bacteria. We are not bringing a new process to the site, we are enhancing a natural process that is already occurring at the site.

References

1. Superfund: The stuff myths are made of. Civil Engineering News January 1990.
2. Bergy's Manual of Determinative Bacteriology, 8th ed. Williams & Wilkins, Baltimore, Maryland.
3. Paul, E. A. and Clark, F. E. In Soil Microbiology and Biochemistry, Academic Press, San Diego, 1989.
4. Bouwer, H. In Groundwater Hydrology. McGraw-Hill, New York, 1978.
5. Dragun, J. Microbial Degradation of Petroleum Products in Soil; In Proceedings of a Conference on Environmental and Public Health Effects of Soils Contaminated with Petroleum Products, October 30–31, 1985, University of Massachusetts, New York, John Wiley & Sons, 1988.
6. Kobayashi, H. and Rittmann, B. E. Microbial removal of hazardous organic compounds. ES&T 16: 170A–183A, 1982.
7. Bumpus, J. A., Tien, M., Wright, D., and Aust, S. D. Oxidation of persistant environmental pollutants by a white rot fungus. Science 228:1,434–1,436, June, 1985.
8. Brock, T. D. In Biology of Microorganisms. Prentice-Hall, Englewood Cliffs, New Jersey, 1979.

9. Freeman, H. M., Ed. In Standard Handbook of Hazardous Waste Treatment and Disposal. McGraw-Hill, New York, 1989.
10. Stanier, R. Y., Adelberg, E. A., and Ingrahm, J. L. In The Microbial World. Prentice-Hall, Englewood Cliffs, New Jersey, 1976.
11. Viessman, W. and Hammer, M. J. In Water Supply and Pollution Control, 4th Ed., Harper & Row, New York, 1985.
12. Moat, A. G. Microbial Physiology. Wiley-Interscience, New York 1979.
13. Dragun, J. In The Chemistry of Hazardous Materials. The Hazardous Materials Control Research Institute, Silver Springs, Maryland, 1988.
14. Grady, C. P. Biodegradation: it's measurement and microbial basis. Biotechnology and Bioengineering 27: 660–674, 1985.
15. Bull, A. T. Contemporary Microbial Ecology. D. C. Ellwood, J. N. Hedger, M. J. Lathane, J. M. Lynch and J. H. Slater Eds., Academic Press, London, 1980.
16. Alexander, M. Biodegradation of organic chemicals, ES&T 19(2), 1985.
17. Atlas, R. M., Ed., Petroleum Microbiology. Macmillan, New York, 1984.
18. Brink, R. H., Biodegradation of organic chemicals in the environmental. In McKinney, J. D. (ed), Environmental Health Chemistry. Ann Arbor, MI.
19. Vogel, T. M. and McCarty, P. L., Transformations of halogenated aliphatic compounds. ES&T 21(8), 1987.
20. Ghosal, D., You, I. S., Chatterice, D. K., and Chakrabarty, A. M. Science 228(4696), 1985.
21. Rittman, B. E., Smets, B. F., and Stahl, D. A. The role of genes in biological processes Part V. ES&T 24(1): 23–29, 1990.
22. McCarty, P. L. Anaerobic biotransformation of chlorinated solvents. Abstract in Biological Approaches to Aquifer Restoration, Recent Advances and New Opportunities. Standford University, 1986.
23. Vogel, T. M. and McCarty, P. L. Abiotic and biotic transformations of 1,1,1-trichloroethane under methanogenic conditions, ES&T 12: 1208–1213, 1987.
24. Kleopfer, R. D. et al. Anaerobic degradation of trichloroethylene in soil, ES&T 19: 277–280, 1985.
25. Parsons, F., Wood, P. R., and DeMarco, J. Transformations of tetrachloroethane and trichloroethane in microcosms and groundwater, AWWA Journal 76: 56–59, 1984.
26. Barrio-Lage, G., Parsons, F. Z., Nassar, R. J., and Lorenzo, P. A. Sequential dehalogenation of chlorinated ethenes. Environ. Science Technol. 20: 96–99, 1986.
27. Cooper, W. J. et al. Abiotic transformations of halogenated organics, 1. Eliminations reaction of 1,1,2,2-tetrachloroethane and formation of chloroethene. ES&T 21: 1112–1114, (1987).
28. Wood, P. R., Lang, R. F., and Payan, I. L. In Groundwater Quality, Ward, C. H. Giger, I. S., and McCarty, P. L., Eds. Wiley & Sons: New York, 1985.

29. Nyer, E. K. and Ziegler, D. Hazardous waste destruction by submerged fixed-film biological treatment. Fifteenth Mid-Atlantic Industrial Waste Conference. 1983.
30. Kemmer, F. N., editor, The NALCO Water Handbook, 2nd edition, McGraw-Hill, New York, 1983.
31. Metcalf and Eddy, Inc., Wastewater Engineering—Treatment, Disposal, and Reuse, 3rd edition, Irwin McGraw-Hill, New York, 1991.
32. Snoeyink, V. L., and D. Jenkins, Water Chemistry, Wiley, New York, 1980.
33. WEF Manual of Practice No. FD-3, Pretreatment of Industrial Wastes, Water Environment Federation, Alexandria, VA, 1994.
34. WPCF Manual of Practice No. FD-8, Clarifier Design, Water Pollution Control Federation, Washington, DC, 1985.
35. Cookson, J. T., Jr., Bioremediation Engineering, McGraw-Hill, New York, 1995.
36. Greene, M., J. Manning, and J. Forbort, Fluid Bed Reactor Study for the Mineralization of DNT, National Environmental Technology Test Sites, Volunteer Army Ammunition Plant, 1997.
37. Wu, Y. C., and E. D. Smith, editors, Fixed-film Biological Processes for Wastewater Treatment, Noyes Data, Park Ridge, NJ, 1983.
38. WEF Manual of Practice No. OM-9, Activated Sludge, 2nd edition, Water Environment Federation, Alexandria, VA, 2002.

4

AboveGround Equipment for In Situ Treatment Designs

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Many in situ cleanups will require aboveground equipment. A common example is an injection system, which necessitates, at a minimum, aboveground pumps and tanks. Land farming, which involves routinely tilling soil, needs aboveground farming equipment to spread the bacteria and nutrients and provide mixing and oxygen. Other than natural attenuation methods, aquifer cleanups will require a minimum of pumps and mixing tanks for the supply of bacteria, nutrients, chemicals, and/or oxygen. Any enhancement that has to be delivered to the contamination zone will require associated aboveground equipment.

In situ cleanups have been the selected method for aquifer cleanups over the last five years.

For applications in which groundwater recovery and aboveground treatment may not be the chosen treatment technology, in situ cleanups are the selected method. With aboveground treatment, the application of treatment technology is engineered and synthetic. Alternatively, with in situ applications, the natural settings and subsurface conditions are utilized, and the treatment technology delivery is a key factor to the success of the application. Given the appropriate conditions, including sufficient site data, adequate site access and treatment positioning, and cost effectiveness, in situ cleanups can be advantageous.

Similar to aboveground treatment technologies, an in situ cleanup design must take into consideration several key factors, discussed in Chapter 1, including flow conditions involved with the injection and recovery of fluids, the concentrations of contaminants and chemicals, and how these parameters change over the course of the remediation (life cycle design). Throughout the remediation timeframe, the influent flow and concentration will change, and life cycle design considers these occurrences to accurately design remediation equipment that will

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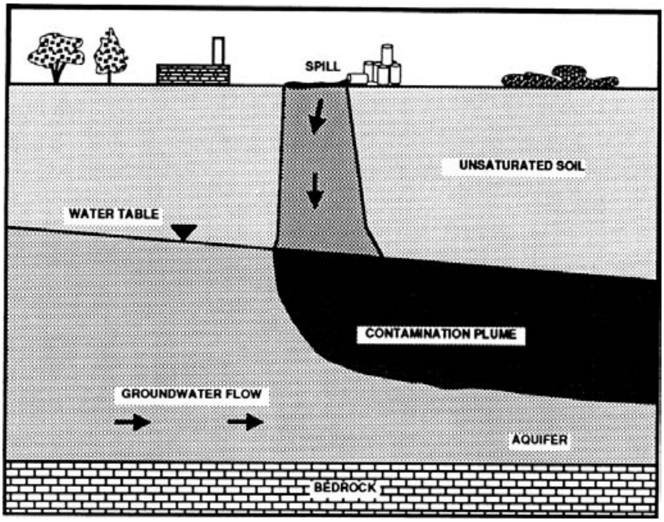

FIGURE 4-1. General view of a contamination plume in the subsurface.

be used not only during remedial action initiation but also throughout the entire duration of the remedial action. Design considerations include equipment in parallel and in series to allow for reduced operation during the second and subsequent years of operation, thereby lowering the costs of electricity and maintenance. The design engineer needs to base the life cycle design implications on an understanding of the site and subsurface conditions.

In situ applications require a thorough understanding of the subsurface environment. Figure 4-1 depicts a general view of a contamination plume in the subsurface. Understanding the components of the subsurface, the water-table elevation and variation, groundwater flow, and contaminant pathways are all a part of the necessary data required to evaluate in situ cleanups.

While historical approaches have generally included the assumption that the distinct lithological units of the subsurface are homogeneous, the identification of *dead zones* and *preferential flow paths* are important to the design of in situ treatment applications.[1] This type of detail, along with a multitude of other details, is necessary to develop a complete conceptual site model. A complete conceptual site model will assure an effective design of treatment applications, including the proper placement of application points, the correct calculations of the amount of materials needed, and the application rate that can be used, based on both the required and achievable delivery rates.

Physical treatment applications involve mass transfer mechanisms to remove contaminants from the soil and groundwater. To effectively accomplish the mass transfer of contaminants from the subsurface, the effective delivery and/or recovery system's design must be used. Aboveground equipment including, but not limited to, air compressors, blowers, pumps, piping, and control mechanisms are necessary to complete the physical removal of contaminant mass from the subsurface.

Biological treatment applications involve enhancing biological growth through the use of nutrients, oxygen, or alternate electron acceptors. To accomplish this enhancement to natural methods, various chemicals, mixing tanks, pumps, blowers, piping, and control mechanisms are necessary to apply the specified treatment. Details of the biological treatment of organic contaminants for aboveground operations were discussed in Chapter 2. The specific parameters required for design are similar; for example, natural in situ microorganisms will require additional oxygen because of the natural organic materials found in most aquifers. These oxidant demand requirements need to be added to the design details for in situ applications.

Chemical treatment applications involve the application of chemicals to react with the specific contaminants of concern at the specific study site. Similar to enhanced biological treatment, in situ chemical treatment requires the use of aboveground equipment, including chemicals, mixing tanks, pumps, blowers, piping, and control mechanisms, to deliver the chemicals to the subsurface. Details of the chemical treatment of organic contaminants were discussed in Chapter 2. Similar design parameters apply; for example, the subsurface environment has natural oxidant demand. Therefore, to provide effective treatment, this key parameter must be included in in situ designs.

DEMAND FOR EFFECTIVE REMEDIATION SOLUTIONS

Since its beginning, the environmental cleanup industry has evolved in many ways to address new needs, as well as new concerns regarding contaminants. The demand for effective remediation solutions is one of these concerns. Early remediation involved the best available technology, and while cleanups proceeded, new research and information surfaced to provide an increased understanding of site conditions and remediation techniques. Additionally, in some instances, site cleanups have required decades to complete, millions of dollars have been spent, and cleanup timeframes have been increasingly scrutinized. Given the history of site cleanups since the 1970s and the increasing costs to conduct a site cleanup, the responsible parties paying for site cleanup and the regulating authorities enforcing site cleanup have become increasingly educated regarding remediation alternatives and cost efficiencies, thereby creating an increased demand for efficient cleanup approaches.

The increased demand is evident in the changes in governmental agency operation and funding throughout the previous decade. Environmental regulatory agencies are being scrutinized more, with cleanup goals established for their programs to ensure effective use of government funds. Typically, the number of sites cleaned up is a metric of program efficiency, but in comparing these percentages across agencies, influential factors affecting the cleanup progress are not completely accounted for.[2]

Historical Perspective

In the initial years of U.S. Environmental Protection Agency (EPA)-directed cleanup efforts, soil excavation and off-site transportation to a landfill or incinerator was the chosen method of source removal. Given the transportation costs and stricter regulations on landfills and incinerators since the late 1980s and 1990s, this method of source removal has become excessive in cost, or cost-prohibitive, for some situations. Additionally, the use of a landfill only removes the contaminated material from the site and concentrates regional contamination in one area; this approach simply moves the contamination from one location to another without destroying the contaminants to remove the potential risk to receptors.

To address groundwater contamination in the early years of site cleanup, groundwater recovery and treatment (also known as *pump and treat*) was the most commonly used technology. The limitations of pump and treat became apparent over years of multiple systems operating and include diminishing returns on the operation of a system that was recovering minimal contaminant mass. Several research groups, including those supported by the U.S. EPA, have conducted pump-and-treat system evaluations to determine the effectiveness of pump and treat and how best to optimize pump-and-treat systems that are either newly designed or have been operating for many years. Pump-and-treat systems are viable alternatives for small, dissolved-phase, fast-moving contaminant plumes; for providing hydraulic containment of a groundwater plume; or where in situ technologies are limited and are not cost effective. Pump-and-treat systems rely on water as the carrier of the contaminant and advection as the necessary process to move plumes. For those instances in which a source material remains in place or low concentrations remain over a widespread area, pump and treat has limitations compared with using an in situ treatment technology in which diffusion is relied on to clean the remaining contaminants in an aquifer.[3,4]

As experience with initial site cleanups increased and additional research regarding subsurface environments concluded, a greater understanding of the delivery requirements and subsequent equipment enhancements evolved. A thorough understanding of the conceptual site model is required to design the effective delivery or recovery systems needed for in situ treatment technology applications.

Conceptual Site Model

The conceptual site model is a complete understanding of the site, including the sources of contamination, the risk to receptors, and how these two could potentially connect. When contaminants are released to the subsurface, the mass of the release, the physical and chemical characteristics of the contaminants, and the subsurface hydrogeology determine how the contaminants move through the subsurface. Figures 4-2 and 4-3 depict the conceptual flow model and the conceptual contaminant transport

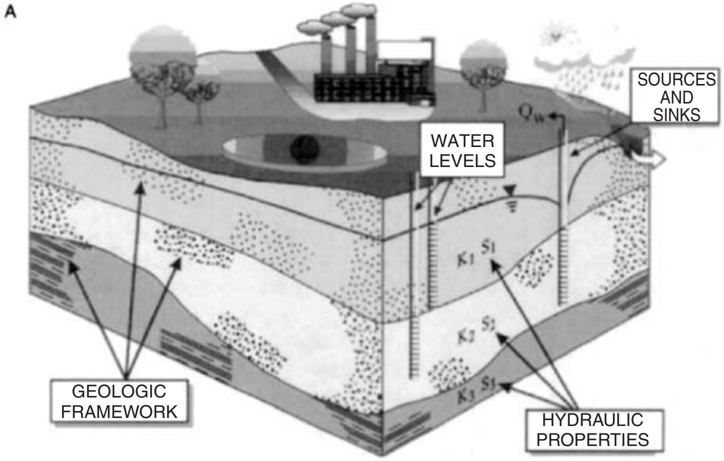

FIGURE 4-2. Conceptual flow model. (Courtesy of Suthersan and Payne, *In Situ Remediation Engineering*, 2005. CRC Press, Boca Raton, Florida.)

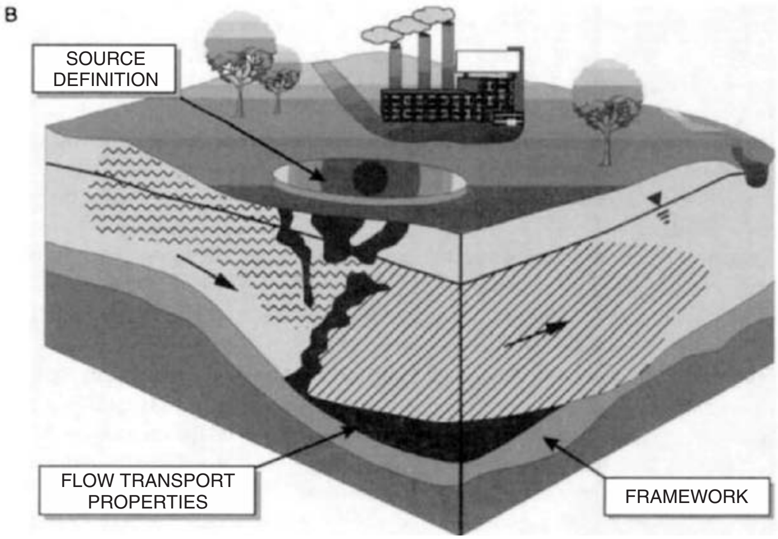

FIGURE 4-3. Conceptual contaminant transport model. (Courtesy of Suthersan and Payne, *In Situ Remediation Engineering*, 2005. CRC Press, Boca Raton, Florida.)

model, respectively. Both are necessary in determining how to design a remediation plan effectively.

The conceptual site model can begin by using regional and local data, available publicly, regarding geographic, geologic, and hydrogeologic information. Additionally, from a review of the site history and aerial photography, the potential source areas can be identified. A complete conceptual site model, however, will require site-specific data and knowledge. Defining all the heterogeneity of a site may be technically unrealistic and/or cost-prohibitive.[1,5]

Expedited site assessment techniques can be used to obtain the needed conceptual site model data in a relatively short timeframe and for a cost-conscious budget.[6,7] The conceptual site model can be completed and should be modified with additional input throughout the entire site cleanup process, including during initial assessment, remediation design, operation and maintenance, and/or natural attenuation monitoring. Guidance for certain situations requiring additional information, such as sites with unexploded ordnance or non-aqueous-phase liquids (NAPL), is available through sources such as the American Society for Testing and Materials and the United States Army Corp of Engineers.[5,7]

The conceptual site model will need to include at a minimum the geology, hydrogeology, and aquifer characteristics of the site. These data should provide answers to such questions as Is the source material in the unsaturated zone, saturated zone or both? Is the aquifer of interest confined or unconfined? Is the soil porous or not, or fractured? The depth to groundwater, groundwater flow direction and rate, and the geochemistry present in the subsurface each affect the evaluation of contaminant fate and migration and assist in determining the level of risk posed by the contamination.

Furthermore, the conceptual site model must include an analysis of the contaminants of concern. The analyses provide an understanding of the chemicals involved, and data regarding the chemical properties can be considered in the overall evaluation of the site. The chemicals may be biodegradable, carcinogenic, hydrophobic, miscible, adsorptive, etc. The properties of the individual chemicals, the synergistic effects of multiple chemicals, and their concentrations are important in determining the level of risk posed by the contamination.

Coupled with the evaluation of subsurface conditions and contaminant properties and concentrations is the distribution of the contamination. Understanding the length, width, and depth of the contamination, as well as the historical and current influences on the subsurface, such as former stream channels, temporal changes, a pumping well for process water, or potable water supply, assists with the evaluation of the level of risk posed by the contamination.

The site characteristics, subsurface conditions, and contaminant properties and concentrations are all necessary to understand the contaminant fate and transport mechanisms, which aid in identifying the risks to receptors. This determined risk and the details of the conceptual site model are important inputs in the evaluation of remediation goals and objectives. Without an adequate conceptual site model, a remediation plan accommodating the necessary delivery or recovery cannot be prepared to provide an effective cleanup.

BIOLOGICAL TREATMENT

Biological treatment is an important technology for the remediation of contaminated sites. Biological treatment is a natural process and is probably already occurring at the site. The main objective of biological remediation designs is to remove any limiting factors in the growth of the bacteria. As bacteria grow in population, the contaminant is used as a food source. The intent is not to provide a new process to remediate the site but only to enhance a natural process that is already occurring at the site.

As reported by the U.S. EPA, over 100 Superfund projects have relied on bioremediation as the main technological approach specified in the sites' Records of Decision. Approximately 55 percent of these projects have relied on in situ bioremediation, whether the natural environment sustained the bioremediation or an enhancement was used.[8] Many of the technologies involved are considered innovative, and multiple new technologies have surfaced to pursue the cost-effective cleanup of various contaminants. Biological treatment involves numerous applications requiring specific monitoring and aboveground equipment to accomplish the remediation goals.

Applications

In situ biological treatment applications include nutrient injection, oxygen enhancement, bacteria growth enhancement, carbon donor injection, and alternative electron acceptor supply, among others. In situ treatment methods require aboveground equipment and can involve ex situ processes as well. For example, a groundwater recirculation process may involve the removal of groundwater, application of nutrients aboveground, and the reinjection of the altered water, which subsequently provides enhancements to the natural environment within the aquifer (Figure 4-4). Each application provides a variety of means to enhance the natural subsurface environment, thereby promoting increased potential for contaminant degradation.

Depending on the aquifer characteristics, either an aerobic or anaerobic bioremediation approach can be instituted. Oxygen enhancement supports an aerobic environment approach. If the subsurface conditions indicate an aerobic environment, then oxygen can be artificially introduced to enhance the growth of natural bacteria.

Biosparging, pure oxygen injection, and sodium percarbonate injection are methods of supplying oxygen to the subsurface. Each method supplies a different concentration of oxygen, and application costs vary, but the core intent is to increase the oxygen supply to grow the bacteria in the subsurface. A comparison of oxygen delivery methods has been evaluated by Nyer et al.[9] These methods are primarily used for aquifer cleanup where the unsaturated zone is not contaminated.

For unsaturated zone cleanup, bioventing is a method of moving air through the subsurface to enhance oxygen supply. Bioventing removes air from the subsurface, thereby allowing air from outside the area of treatment to enter the area of treatment. This "new" air ideally contains higher concentrations of oxygen, which provides bacteria with oxygen

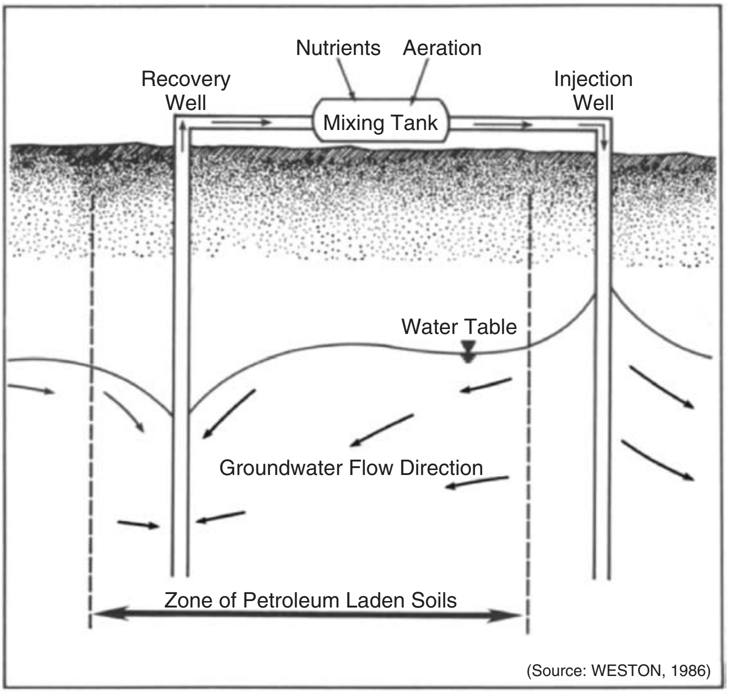

FIGURE 4-4. The groundwater recirculation process. (Courtesy of *USEPA 2004*.)

to sustain growth, thereby supporting the continued degradation of contaminants.

Nutrient injection accomplishes bacterial growth by providing the nutrients determined to be missing or limited in the subsurface environment. Nutrient injection can be applied in an aqueous or gaseous phase. The conceptual site model or remediation planning support should include the collection of samples to evaluate the existing nutrient supply in order to provide nutrients that will enhance the growth of the existing bacteria. Nutrients such as nitrogen are common elements in limited supply in the subsurface. Along with oxygen, these nutrients provide bacteria with the means to grow.

Anaerobic bioremediation techniques include the use of alternative electron acceptors and carbon substrate for bacterial growth. The substrate is the food on which bacteria grows. Certain substrates are better suited for bacterial growth than others. For chlorinated compound contamination, reductive dechlorination, which involves enhancing bacterial growth to pursue faster breakdown of compounds such as perchloroethene and trichloroethene through removal of each chlorine element ending with ethene, is one method. Ethene can be further reduced to carbon dioxide and water, which completes the mineralization process. This approach is suitable for sites where subsurface conditions allow adequate application of the organic carbon substrate. Substrates used for anaerobic bioremediation enhancement include fluids such as lactate, molasses, and vegetable oils.[10] In situ bioremediation of DNAPL source areas can also be implemented at project sites if the appropriate conditions are present, the application timing is agreeable, and the cost-effective analysis indicates the application should be chosen.[11]

Each application technique requires a variety of monitoring to measure the performance of the delivery and technology application. Performance measures include confirmation of the in situ application throughout the treatment area and degradation of the contaminants. Certain monitoring tools are used for all in situ applications; however, additional monitoring approaches that are unique to the application technology should be applied.

Monitoring

Application monitoring is required for all remediation techniques. At a minimum, contaminant degradation or confirmation of the absence of contamination, such as in excavation of contaminated soil, is conducted. Additional monitoring should be tailored to the remediation approach to confirm that remediation is implemented as planned. Baseline monitoring prior to remediation should include the planned performance monitoring parameters. If the injection of bioremediation enhancement fluids is not achieving complete delivery to the entire area of contamination, then additional injection may be required. Therefore, sampling a representative number of monitoring wells within and surrounding the treatment area for the parameters used to indicate the presence of the injection fluid is necessary.

Bacteria survive and thrive if the conditions are appropriate. The routine monitoring should include parameters such as pH, temperature, and dissolved oxygen concentration, which can be field-tested at the project site. If these parameters change to conditions that do not support bacterial growth, then the injection of fluid to enhance the growth will not produce successful results within the planned timeframe.

Physical collection and analysis of these data can involve a variety of equipment, timeframes, and costs. Field measurement can be completed using portable tools such as a water-quality meter, a water-level meter, and pressure gauges. The water-quality meter includes probes that measure the in situ pH, dissolved oxygen concentration, redox potential, and temperature. Automatic data collection and logging can be accomplished using probes that are installed in monitoring wells for an extended period of time. These probes collect similar information along with barometric pressure. Use of some bioremediation enhancement fluids can cause the creation and emission of gases during reactions in the subsurface. Therefore, monitoring for gases and/or pressure buildup is an important safety concern, as well as an appropriate indicator of reaction processes.

Monitoring before and during remediation implementation allows for measuring of progress and determining where remediation success is present. Adjusting the remediation application to accommodate nontreated areas and reducing the application area based on cleanup progress are part of the optimization of the remediation treatment.

Equipment

Each in situ biological remediation application requires aboveground equipment. Whether this equipment is placed at the project site and remains or the equipment is mobilized to the site on a routine basis for short-term applications, a variety of equipment is available for use.

Applications involving the continuous injection of air or fluid and/or recirculation of groundwater require the installation of permanent infrastructure and equipment aboveground to maintain the application. Depending on the goals and objectives of the remediation application and the timeframe and budget available, a variety of equipment may be specified to accomplish these goals and objectives.

Recirculation of groundwater involves the extraction, treatment, and reinjection of groundwater. These processes require groundwater extraction pumps, either submersible or aboveground, process piping and pumps, treatment units, and control mechanisms. The treatment units will include a reaction vessel, which may be a closed tank, open-top tank, or surface impoundment (see Figure 4-4).This treatment vessel will be used for four main functions:

1. To produce bacteria
2. To reduce organic content of the water
3. To add oxygen to the water
4. To add nutrients to the water

Bacteria are the workhorse of an in situ cleanup. Large quantities of bacteria are required for the process. Natural bacteria are usually sufficient for most cleanups, but an aboveground biological unit can increase the rate of cleanup. A standard biological treatment system can be set up aboveground. The system can be a lagoon, activated sludge, or fixed-film system, depending on the amount of bacteria required. Bacteria will produce at a rate of between 0.10 and 0.25 pound of bacteria per pound of organic consumed. Any of the biological treatment systems discussed in the previous chapters are very effective in growing the required bacteria. The choice between the systems will be made mainly on the amount of bacteria required and the concentration of contamination allowed to be recharged to the aquifer. Lagoons produce the highest quantity of bacteria per pound of organic consumed. However, lagoons produce too high a concentration of bacteria when a well recharge is to be used. The bacteria can clog the well. Activated sludge or fixed-film systems produce the highest quality organic effluent content. Activated sludge or fixed-film systems with a clarifier will both discharge lower concentrations of bacteria. Settled bacteria in the clarifier can be added to the recharge water to obtain the desired bacterial concentration.

The food for the bacteria is readily available. The primary well will be in the center of the plume. The contaminants will be at their highest concentration at this point. The water drawn from the well is sent to the treatment tank, and the bacteria grow on the contaminants. This will produce bacteria that are actively degrading the compounds found in the aquifer. The same holds true for compounds flushed from the unsaturated zone.

The reaction tank accomplishes the second function simultaneously with the first function. The bacteria use the contaminants found in the groundwater for food. As they use the compounds, the organics are removed from the water. The recharge water has the bacteria in it, but not the original contaminants. The recharge water should not exhibit a high concentration of the contaminants.

The final uses of the aboveground reaction tank are to supply nutrients and oxygen. The nutrients are added to the tank. Enough nutrients must be added to satisfy the requirements of the biological reaction within the tank and to have a residual for the recharge water. The same is true for oxygen. The discharge concentration of oxygen from the reaction tank should be near the saturation level. This is true even if hydrogen peroxide is used as an additional oxygen source.

While in situ treatment will lower the cost of the project and speed its completion, the rate of biological destruction is always faster in an aboveground tank because oxygen and nutrients can be readily supplied. Any contaminants that can be destroyed aboveground should be. Also, the bacteria will be "hungry" for more food if they are reintroduced to the ground. Removal of the contaminants will also minimize the oxygen requirements below ground.

Batch applications of injection fluid on a routine basis can be accomplished using a mobile treatment setup, wherein a tank, pump, and associated appurtenances are used. Figure 4-5 depicts the configuration of a batch injection setup. If a gaseous fluid is being injected, an air compressor or blower may substitute for the pump. The associated appurtenances required for this setup include valves, piping or hoses with quick-connectors to allow ease of connection and disconnection, and gauges to monitor the system and progress of the application.

The control mechanisms required for fixed and mobile systems include valves for controlling fluid flow rates, flowmeters to check the application against the design, and pressure gauges to monitor pressure buildup. These controls provide varying protection and monitoring of the injection progress. The valves can be adjusted to allow varying delivery flow rates or to completely stop the flow of fluid. Flowmeters provide a performance monitoring mechanism used to determine how the actual delivery flow compares to that expected during the remediation design and can be used to track the total volume of fluid injected into each injection point. Pressure gauges are used to monitor the pressure at various points in the system. The pressure buildup observed at the injection point is compared to the injection pressure from the design and is also used to determine if a problem is occurring with clogging of the injection point screen or in the aquifer.

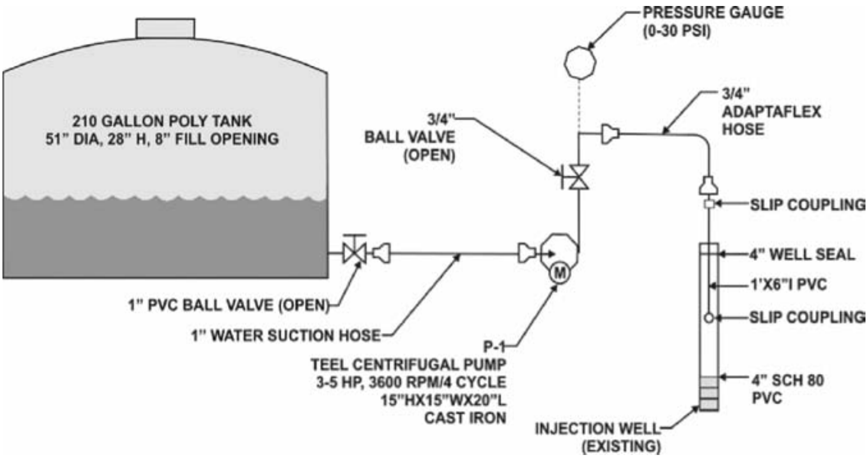

FIGURE 4-5. The batch injection configuration. (Courtesy of AFCEE 2004.)

In fixed systems, these control mechanisms may be connected to a programmable logic controller and interlocked to allow automatic operation that will prevent personnel, equipment, and environmental damage. For example, level controllers are required to shut down the supply pumps to prevent spillage of the vessel contents. These controls will be interlocked with the upstream process equipment to prevent equipment damage and spillage of additional vessel contents, such as bacterial or nutrient supply vessels. With mobile systems, these controls may be installed, but more reliance on the equipment operators to control these possibilities is needed.

CHEMICAL OXIDATION

In situ chemical oxidation involves injecting a chemical to react with the contaminants in the subsurface, causing a breakdown of the contaminants to harmless end products such as carbon dioxide and water. Numerous chemicals have the ability to react with contaminants of concern at a project site. The chemical reactions that are planned occur in relatively short timeframes, which is one advantage of chemical oxidation—the quick cleanup of sites. The important issue is whether those chemicals have the potential to produce harmful by-products, dangerous exothermic reactions that can result in a health and safety issue, or conditions that could corrode underground structures and utilities.

Chemical oxidation is primarily an aquifer treatment, but the unsaturated zone can be treated with a chemical oxidation solution. Similar to biological treatment, the appropriateness of chemical oxidation at a project site will depend largely on the subsurface conditions and whether the chemicals can be delivered effectively to reach the contamination. The majority of the chemical oxidation techniques require short timeframes. If the groundwater pH is greater or less than the range of 7 to 9, the chemical oxidation injection effectiveness can be greatly reduced, depending on the injection material. Additionally, the oxidant demand of the soil and groundwater needs to be accounted for in the planning. If the chemical oxidant demand is calculated solely on the concentrations and oxidant demand of the contamination, the natural organic matter and minerals may interfere with the planned chemical reactions, and complete breakdown of contaminants will not occur. Raw materials including the chemical supplies are shipped to the project site, mixed on-site into a solution, and injected through temporary injection points or injection wells.

Handling of raw materials and use of chemical oxidation techniques in general raises numerous health and safety concerns. Raw materials can be supplied in solid or liquid form, and the oxidative nature of the raw materials presents concerns for reactivity, dust, and corrosiveness. For batch applications, only the amount of raw materials needed for each batch should be supplied to the site. Storage of raw materials may involve ensuring proper ventilation, shading from sunlight, protection from rain, and separation from other materials that may be reactive with the chemical. For continuous applications, these concerns for raw material storage must be planned as part of the remediation design. Additional health and safety concerns arise from the fact that many chemical reactions produce heat. Finally, one additional concern is the potential reaction the various chemicals may have on metallic underground utilities. Damage to underground utilities can cause additional health and safety concerns, as well as concerns with nonoperation and repair of the utility.

In situ chemical oxidation techniques rely on the oxidative ability of certain compounds. A summary of oxidant strengths relative to chlorine is included as Table 4-1.

The hydroxyl radical is the strongest oxidant, but the reaction rate for the hydroxyl radical is nearly immediate. The hydroxyl radical is formed when either ozone or hydrogen peroxide decomposes. To affect an adequate area of the subsurface, closely spaced injection points are needed and either an alternative oxidant or a solution that breaks down to provide the oxidant is used. Weaker oxidants can persist in the subsurface, thereby allowing longer reaction times or influence farther from the injection point. Numerous applications have developed over the previous decade, but a few applications have sustained progress in accounting for the concerns mentioned.

TABLE 4-1 Oxidant Strengths

Chemical Species	Standard Oxidation Potential (volts)	Relative Strength (c*hlorine* = 1)
Hydroxyl radical($OH^{-\bullet}$)[a]	2.8	2.0
Sulfate radical ($SO_4^{-\bullet}$)	2.5	1.8
Ozone	2.1	1.5
Sodium persulfate	2.0	1.5
Hydrogen peroxide	1.8	1.3
Permanganate (Na/K)	1.7	1.2
Chlorine	1.4	1.0
Oxygen	1.2	0.9
Superoxide ion ($O^{-\bullet}$)[a]	−2.4	−1.8

Source: ITRC, 2005

[a] These radicals can be formed when ozone and H_2O_2 decompose.

Applications

Common in situ chemical oxidation applications include Fenton's reagent, ozone, permanganate, and persulfate, among others. Each application has various advantages and disadvantages, as outlined in the following paragraphs.

Fenton's reagent application involves using hydrogen peroxide and ferrous iron, which react to form the hydroxyl radical. The use of this approach requires a low pH environment, which likely requires the addition of chelating acid or by acidifying the hydrogen peroxide.[12] Fenton's reagent application is not suitable in subsurface conditions involving limestone because of the basic condition (high pH) of the aquifer and the fact that carbonate compounds will react with the hydroxyl radical before the contaminants have the opportunity.

Fenton's reagent applications have a high potential for increased risk of fugitive vapors, reaction by-products, precipitation of metals in the subsurface, and groundwater plume migration. Fugitive vapors can form based on the exothermic reactions involved with the use of this application; the reactions heat up the groundwater in the subsurface and have the potential to produce steam. If the vapors that are produced are not collected or controlled, then concerns arise associated with vapor intrusion into buildings and vapor migration through underground utility corridors. Buildup of vapors below ground can provide an explosive environment as a result of the pressure buildup. One method of controlling these vapors is to install a vapor extraction system.[4]

Permanganate is another common oxidation application. Sodium permanganate or potassium permanganate can be used to address organic contamination. Sodium permanganate is typically supplied in liquid form, while potassium permanganate is available more commonly in solid form. One concern with these applications is the potential impurities found in the supplies, including metals, salts, and silica. These impurities can provide a potential disadvantage when compared to other oxidation techniques because of the elevated concern of clogging a well screen or aquifer, thereby reducing effective delivery to the contaminants. Alternatively, when compared to Fenton's reagent, permanganate can be used in subsurface conditions involving a wider pH range (i.e., the application does not require low pH to be effective).

Another advantage of permanganate solutions is the stability of the oxidant in the solution. Increased stability allows for increased delivery and distribution within the aquifer and direct contact with additional contaminant volume. Furthermore, permanganate has been shown to be an effective treatment for source areas containing DNAPL.

A third oxidant experiencing increasing application is persulfate. Persulfate is typically supplied in solid form and requires an activator such as heat, hydrogen peroxide, high pH, or a metal chelating agent. Persulfate salts available commercially include ammonium persulfate, sodium persulfate, and potassium persulfate. Depending on the site conditions and potential groundwater concentrations of precipitated elements, the chemical application may produce alternative groundwater contamination concerns.

The raw material persulfate salts break down to produce the persulfate anion, which is a strong oxidant. The activator produces sulfate free radicals, which are similar to the hydroxyl radical in that they are strong oxidizers and react rapidly.

Monitoring

Similar to biological treatment applications, chemical oxidation methods require monitoring to ensure delivery and treatment effectiveness. Prior to considering chemical oxidation, an understanding of the contents of the target aquifer is a necessity. Knowing what metals are present, as well as the oxidant demand of the soil and groundwater, is key to determining the total oxidant demand for the design and ensuring that metals contamination will not be enhanced through the application of a chemical oxidation technique. Throughout the application, performance monitoring is required to enable the evaluation of the application's success.

At a minimum, contaminant monitoring will allow an analysis of the degradation progress of the contaminants. Injection protocols usually require some form of approval from an Underground Injection Control agency. The Underground Injection Control group will specify certain monitoring requirements specific to the chemicals planned for injection.

Depending on the oxidant used for an application, the elements that require monitoring may include the elements of the salt, total dissolved solids for general elements that dissociate from the oxidant solution, specific metals, and by-products of the anticipated final reactions of the oxidation application. Along with the specific parameters of an application, general parameters that require monitoring include temperature, pH, and pressure buildup in the aquifer. Additionally, monitoring dissolved oxygen concentration may be appropriate if the application includes increased oxygen following completion of the chemical oxidation reactions. Considering the health and safety of the operators and the general public, as well as the potential for undesirable media coverage, an explosimeter may be required to monitor for explosive conditions.

Potassium permanganate applications have a unique parameter that can be monitored. The solution produces a purple hue when mixed and applied. Therefore, a purple tint in the groundwater from downgradient monitoring wells will be an indication of the presence of unused potassium permanganate. The absence of a purple tint in downgradient monitoring wells will indicate that the permanganate solution has been consumed. In this case, depending on the contaminant concentrations and the distance from the injection wells, additional applications may be required to ensure the solution is delivered and distributed sufficiently.

As with any remediation application, monitoring of the performance aspects allows an evaluation of the success of the application. Given the present and relative high cost of site cleanup, adequate monitoring provides a means to focus treatment on remaining contamination, thereby reducing the wasteful application of additional chemicals throughout the entire area of initial contamination. This leads to cost savings and time benefits.

Equipment

Each in situ chemical oxidation remediation application requires aboveground equipment to deliver the application to the subsurface. Careful consideration of the equipment planned for use with the various chemicals of a chemical oxidation application is a necessity. The general equipment used (pumps, tanks, compressors, blowers, etc.) is similar to those items discussed in the previous section on biological treatment; however, depending on the chemicals being used, chemical compatibility issues arise. For example, stainless steel and Schedule 40 PVC piping are recommended for the injection of sodium persulfate, while high-density polyethylene (HDPE) or Schedule 80 PVC may be appropriate for other applications. Given the acidic nature of some chemical oxidation applications, use of metal piping other than stainless steel or reuse of piping that may have integrity issues becomes a major concern.

The raw materials can be supplied in a variety of methods, from small 5-gallon buckets to a stainless-steel tanker truck. The purpose of the vessels varies from simple storage of the raw materials to actually mixing raw materials in preparation for injection. Depending on the application reaction timeframe, raw materials may be stored separately aboveground and mixed in situ to allow distribution during reaction, thereby lessening potentially wasteful reaction time during delivery. For immediate reactions, this approach is necessary to be effective. If sufficient distribution does not occur in a timely manner, the oxidation does not reach the contamination and may prove detrimental to future remediation (e.g., where a precipitate forms and fills the pore space of an aquifer). Similar to an epoxy adhesive, the two chemicals remain separated until the location of treatment is reached, where the combination and reaction of the chemicals provides a distinct result.

For the most part, in situ chemical oxidation strategies involve mobile equipment, which is set up at the project site for a temporary period of time and removed when the injection is complete. A recirculation strategy is one application where fixed aboveground equipment would be required. Fixed system components require enhanced health and safety protection measures. For example, emergency plans for a chemical spill or leak from a fixed pipe, eyewash stations for splash incidents, and notification procedures for the instance of pressure buildup and/or gas releases may be required for a recirculation application.

Enhanced control mechanisms should be instituted, whether the application is a fixed system or a mobile unit. Redundant control mechanisms, including backup pressure relief valves, spill containment procedures, and increased training, are examples of the enhanced control measures that should be used to provide a safe work environment. Given the potential dangers discussed above, including pressure buildup, acidic conditions, and heat or steam generation, the application operators require complete training regarding the health risks and personal protective equipment required to conduct these applications. Chemical gloves, dust masks, or face shields and aprons may be needed, depending on the application. The Material Safety Data Sheet (MSDS) for each chemical includes specific personal protective equipment for handling the chemical.

PHYSICAL TREATMENT

Physical treatment involving mass transfer from contaminated media is the original approach for contaminated site cleanup. In the initial site cleanups beginning in the 1970s, excavation and groundwater pump-and-treat systems were the main approaches to the cleanup of soil and groundwater, respectively. Upon initiation of “innovative” technologies, physical treatment continued to be heavily favorable. These in situ approaches rely on the physical removal of contaminants from the subsurface either through recovered liquid, vapor, or both. Physical treatment involves numerous applications requiring specific monitoring and aboveground equipment to accomplish the remediation goals.

Applications

In situ physical treatment applications include air sparging, vapor extraction, and multiphase extraction, among others. The liquid (groundwater) to the vapor phase mass transfer used in these technologies includes inducing fluid flow toward recovery points. These technologies are most applicable to VOCs that include those chemicals with vapor pressures generally in the range of 0.5 to 1.0 millimeters of mercury (mmHg). Each application is appropriate to varying site-specific conditions, including subsurface lithology and contaminant properties. Based on the cumulative effect of these conditions, along with consideration for surface operations and the aspects of each aboveground treatment technology, a cost–benefit analysis needs to be completed to determine which technology is applicable.

Air sparging and vapor extraction rely on air as the contaminant carrier to effectively remove mass from the subsurface. In coarse-grained soils, the permeability is high, and sufficient airflow is achievable to support the cost–benefit of these technologies. Multiphase extraction involves the collection of air, water, and, in some cases, NAPL. Multiphase extraction is more appropriate for a site when NAPL is present or the subsurface soils are lower permeability, such as clayey materials. Depending on the depth of the contamination and the affected media, excavation or pump and treat may remain the cost-effective approach. These technologies have been used for the majority of site cleanups in the United States and continue to be used currently when the site conditions indicate the appropriateness of these technologies.

Each application technique requires a variety of monitoring to measure the performance of the delivery, recovery, and technology application. Performance measures include confirmation of the in situ application throughout the treatment area, degradation of the contaminants, and mass recovery monitoring.

Monitoring

Application monitoring for physical treatment technologies includes the contaminant degradation (or absence of contamination as in an excavation) in the affected media. Physical treatment technology applications often involve monitoring the mass removal efficiency. Mass removal technologies may reach an asymptotic level of removal, and the costs associated with operation and maintenance of a continuing remediation system reach diminishing returns based on the minimal amount of mass being removed. Additionally, the primary phenomenon involved is mass transfer; the mass is simply being moved from one phase to another and concentrated, and a discharge to air, water, or both is continuing aboveground. Therefore, monitoring requirements are placed on the discharge to ensure that a subsequent medium is not being contaminated at concentrations greater than allowable.

Routine operation and maintenance monitoring involves a variety of flowmeters, control valves, totalizers, and pressure and vacuum gauges. Routine operation and maintenance serves the following purposes: (1) measuring technology performance, (2) identifying troublesome operations, (3) performing routine maintenance of aboveground equipment to sustain long-term operability, and (4) determining how and when to optimize system operation to focus the treatment on the remaining contaminated areas.

Equipment

A variety of aboveground equipment is available for in situ physical treatment technology applications. Equipment selection, including appropriate appurtenances, is uniquely associated with the designed operation. Depending on the design pressure, airflow, operation timing, and lifetime of the remediation need, a wide variety of air compressors, blowers, pumps, and ancillary equipment may be applicable. Each equipment component has select operating curves, optimum performance ranges, and disadvantages and advantages compared with another similar piece of equipment. The design engineer will need to weigh these issues against costs, time constraints, and site or regulatory constraints.

Several types of air compressors are available to provide the design air injection pressure and flow rate needed to deliver air into the subsurface.[3] Chapter 5 of the reference summarizes power ranges, pressure ranges, and advantages of common air compressors. Several equipment manufacturers and vendors have catalogs or information on the internet available for common air compressors as well.

The complementary component to an air sparging system is often a vapor extraction system. If the designed physical treatment application involves stripping contaminants from the groundwater and capillary fringe, then a system to recover those stripped contaminants is necessary to avoid contaminant migration in the vapor phase. A vapor extraction system is essentially a multiphase extraction system designed to recover primarily vapors. While the vapor extraction system is designed to recover minimal groundwater, the multiphase extraction system targets the recovery of groundwater as one of the main mass transfer components of this physical treatment technology. Therefore, with a multiphase extraction system, mass transfer is occurring in both the liquid and air phases, and if applicable, as recovered NAPL. As with air compressors, a variety of air blowers and vacuum pumps are available for numerous site conditions. Based on operating curves for various vacuum pumps, including liquid-ring pumps, rotary vane, rotary piston, rotary lobe, and regenerative blowers, as well as ejectors, the design engineer determines which type of vacuum pump is best-suited for the application.[1] For example, for sites where a high vacuum (greater than 15 inches of mercury [inHg]) and high airflow are needed to achieve site cleanup, a rotary piston blower or a liquid-ring pump is appropriate. From this identification, the design engineer can then narrow the analysis of the advantages of each type of equipment to determine which will provide effective recovery for the site-specific situation.

SUMMARY

Most in situ cleanups will require aboveground equipment. Additional in situ treatment methods not detailed in this chapter include vapor extraction systems, fracturing, iron injection, and phytoremediation, to name a few. Whether the aboveground equipment is portable or fixed in place at the site, aboveground equipment is required to affect the subsurface. Regardless of the chosen technology, the commonalities in design include the factors discussed in Chapter 1 and the fact that some type of aboveground equipment will be required.

References

1. Suthersan, S., and F.C. Payne, In-situ Remediation Engineering, CRC Press, Boca Raton, Florida, 2005.
2. Terwilliger, T.A., Petroleum Cleanup in the United States: a Historical Review and Comparison of State Programs, Thesis, University of South Florida, Tampa, Florida. October 2006.
3. Nyer, Evan K., et al., In-situ Treatment Technology, 2nd edition, 2001.
4. United States Environmental Protection Agency, *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites*, EPA-51-R-004-02, May 2004.

5. United States Army Corp of Engineers, *Conceptual Site Models for Ordnance and Explosives (OE) and Hazardous, Toxic, and Radioactive Waste (HTRW) Projects*, EM 1110-1-1200, February 3, 2003.
6. United States Environmental Protection Agency, *Expedited Site Assessment Tools for Underground Storage Tank Sites*, EPA 510-B-97-001, March 1997.
7. American Society for Testing and Materials, *Standard Guide for Developing Conceptual Site Models for Contaminated Sites*, ASTM E1689-95, 2008.
8. United States Environmental Protection Agency, *Use of Bioremediation at Superfund Sites*, EPA 542-R-01-019, September 2001.
9. Nyer, Evan K., J. Scott Davis and Isabel King, Oxygen revisited, *Groundwater Monitoring and Remediation*, Summer (2002).
10. United States Air Force Center for Environmental Excellence, *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*, August 2004.
11. Interstate Technology & Regulatory Council, *In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies*, April 2007.
12. Interstate Technology & Regulatory Council, Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd edition, ITRC, Washington, DC, January 2005.
13. United States Army Corp of Engineers, *Groundwater Hydrology*, EM 1110-2-1421, USACE, Washington, DC, February 28, 1999.

5

Treatment Methods for Inorganic Compounds

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The main inorganic contaminants found in groundwater include the following:

- Heavy metals
- Arsenic
- Barium
- Cadmium
- Trivalent chromium
- Hexavalent chromium
- Copper
- Lead
- Mercury
- Nickel
- Silver
- Zinc
- Nitrates
- Perchlorate
- Sulfates
- Total dissolved solids
- High and low pH

Inorganic contaminants in groundwater have not received as much attention as the organic contaminants for several reasons. First, the unsaturated ground, or vadose zone, has an ability to remove these contaminants from a spill so that they reach the aquifer in only limited quantities. Most soils have an ion exchange capacity. For example, a heavy metal moving through the soil will be exchanged with a cation in the soil and be adsorbed by the soil. In addition, anaerobic zones in the soil can biologically transform nitrates into nitrogen gas. The soil also has a natural ability to neutralize pH to a limited extent.

Inorganic compounds are also not used as frequently as organic compounds for industrial purposes. Industrial plants do not usually keep heavy metal solutions in large storage tanks, and pipelines are not typically used to transfer these compounds. Heavy metals in their pure state are not soluble in water. Even when stored as a salt, which is soluble in water, they are in a solid form. Unlike gasoline storage tanks,

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oil pipelines, or solvent storage tanks, there are no similar storage or transfer facilities for inorganic compounds.

One of the largest sources of heavy metals contamination is leachate from abandoned waste disposal sites. Legal landfills, illegal landfills, and old mines are probably the major sources of heavy metals contamination. Ten years ago, the regulations did not anticipate the problems caused by the improper burial of heavy metals.

Another significant source of metals contamination is transient, geogenic compounds, which are naturally occurring compounds released from the soil matrix as a result of a change in the environmental conditions. A changed environmental condition may occur as a result of the release of organic compounds, causing a naturally aerobic aquifer to become anaerobic.

The largest source of arsenic, nitrates, and total dissolved solids contamination is agricultural chemical usage. These sources represent low concentration material being introduced into the ground. Chemicals used for agriculture are also a source of organic contaminants, mainly pesticides.

Low concentrations of nitrates have long been known to cause methemoglobinemia in infants. Recently, the public has recognized that other low concentrations of inorganic compounds are also unacceptable because of health concerns. This awareness, combined with the cleanup of abandoned sites, has moved inorganics into the forefront.

This chapter covers the following methods for the removal of inorganics from groundwater:

- Chemical addition
- Removal of suspended solids
- Membrane technologies
- Ion exchange

A major advantage of developing treatment methods for inorganics in groundwater is that most of the methods described in this chapter can be tested in the laboratory. The results can be accurate enough to develop a preliminary design of the full-scale system; however, pilot studies should be conducted for any of the methods that use membranes, i.e., reverse osmosis. Pilot studies may also be warranted if a “mixed bag” of contaminants requires removal. The laboratory test for inorganic compounds can also be performed in a short period of time, days rather than the weeks and months that it takes to get good data for organic treatment methods. All of the methods listed in this chapter should be tested at several different concentrations and pH ranges. All water is slightly different, and while dosages and pH are recommended in the text, the optimum conditions will have to be found for treating each groundwater.

CHEMICAL ADDITION

pH Adjustment

There are two main purposes for pH adjustment in the treatment of groundwater. The first is to adjust the groundwater to a neutral pH of around 7; water that is to be discharged to a receiving stream must have a pH between 6 and 9. The second is to precipitate the heavy metals. While precipitation normally includes an adjustment of pH, other chemical additions are necessary when removing chemicals such as arsenic, barium, and hexavalent chromium. This is covered in the next section.

In wastewater treatment, the preferred method of pH adjustment is to merge two waste streams of differing pH. During groundwater treatment, a secondary source for pH adjustment is usually not available. Therefore, the main methods used for the adjustment of acidic water include the following:

- Passing the groundwater through a limestone bed
- Mixing the groundwater with lime slurries
- Adding caustic in the form of sodium hydroxide or potassium hydroxide to the groundwater
- Adding soda ash to the groundwater

The main methods for adjusting alkaline water are the following:

- Bubbling carbon dioxide in the water
- Adding a strong acid such as hydrochloric acid or sulfuric acid

It is very rare for a groundwater to be too alkaline. The main reason for adding acids to a groundwater is for pH readjustment after the water has been raised to a high pH to precipitate a metal. The addition of a strong acid is the typical method used for this adjustment. The proximity of an industrial plant impacts the cost effectiveness of adding carbon dioxide.

It should be noted that aeration treatment methods for the removal of VOCs (i.e., air stripping, diffused aeration) will liberate carbon dioxide and slightly raise the pH of groundwater. Generally, the pH adjustment is a unit or less (i.e., from pH 7 to pH 8).

Depending on the final pH level required, lime can take up to 30 minutes to react and be completely used. The slurry should be introduced to the acidic groundwater in a completely mixed tank, and residence time in the tank should therefore be at least 30 minutes. (Once again, this number does not represent a hard design number. The actual reaction time should be tested on each groundwater.) This slow reaction time will make pH control more difficult. Lime will also form more sludge than neutralizing with caustic, primarily because of the precipitation of calcium carbonate. For every 1 milligram (mg) of calcium precipitated from the groundwater, 2.5 mg of calcium carbonate sludge will be generated.[1]

Caustic can be delivered and stored as a liquid. The reaction time for caustic is very fast. The reaction tank should still be completely mixed, and about 5 to 10 minutes of residence time is usually sufficient. Caustic can be used at several different concentrations. This can be an advantage for small streams that are near neutral pH. Short-term (1- to 2-year) groundwater treatment projects will probably use caustic for pH adjustment. Long-term projects may take advantage of the low cost of lime.

Chemical Addition for Precipitation

The removal of heavy metals from the groundwater by precipitation is governed by the solubility of the metal when combined with anionic species such as hydroxide, carbonate, and sulfide. These are the most common anionic conjugates for metals precipitation; however, other anions can be used, such as sulfate for the precipitation of barium.

The solubility of cationic metal species with various anions is described by a constant called the solubility product, or K_{sp}. Table 5-1 provides a listing of solubility products for a variety of metal cation–anion combinations. The solubility product constant is described by the following equation:

$$K_{sp} = [\mathrm{Me}^{+}][\mathrm{An}^{-}]$$

where

K_{sp} = the solubility product constant
$[\mathrm{Me}^{+}]$ = the concentration of a metal cation in solution in moles per liter
$[\mathrm{An}^{-}]$ = the concentration of a corresponding anion in solution in moles per liter

TABLE 5-1 Solubility Product Constants

		$K_{sp}{}^{a}$ (64–77°F)	$K_{sp}{}^{b}$ (25°C)	$K_{sp}{}^{c}$ (25°C)	$K_{sp}{}^{d}$ (25°C)	$K_{sp}{}^{e}$ (25°C)
Maganous sulfide		1.4×10^{-15}				
Ferrous sulfide	FeS	3.7×10^{-19}	6×10^{-19}	8×10^{-19}	4.9×10^{-18}	
Zinc sulfide	ZnS	1.2×10^{-23}	2×10^{-25}		2.0×10^{-25}	
Nickle sulfide	NiS	1.4×10^{-24}	3×10^{-19}	4×10^{-20}		
Stannous sulfide		1.0×10^{-25}				
Cobalt sulfide	CoS	3.0×10^{-26}	4.0×10^{-21}	5×10^{-22}		
Lead sulfide	PbS	3.4×10^{-28}	3×10^{-29}	3×10^{-28}		
Cadmium sulfide	CdS	3.6×10^{-29}	8.0×10^{-27}	1×10^{-27}		
Silver sulfide	Ag_2S	1.6×10^{-49}	6×10^{-51}	8×10^{-51}	1.0×10^{-49}	
Bismuth sulfide		1.0×10^{-97}	1×10^{-97}			
Copper sulfide		8.5×10^{-45}				
Mercuric sulfide		2.0×10^{-49}				
Aluminum hydroxide	$Al(OH)_3$		4.6×10^{-33}	3×10^{-34}	1.9×10^{-33}	1.9×10^{-33}
Aluminum phosphate	$AlPO_4$		6.3×10^{-19}	9.84×10^{-21}	1.3×10^{-20}	9.8×10^{-21}
Barium bromate	$Ba(BrO_3)_2$			2.43×10^{-4}		
Barium carbonate	$BaCO_3$		5.1×10^{-9}	2.58×10^{-9}	8.1×10^{-9}	
Barium chromate	$BaCrO_4$		2.2×10^{-10}	1.17×10^{-10}	2.0×10^{-10}	1.2×10^{-10}
Barium fluoride	BaF_2		1.0×10^{-6}	1.84×10^{-7}	1.7×10^{-6}	1.8×10^{-7}
Barium hydroxide	$Ba(OH)_2$		5×10^{-3}			5.0×10^{-3}
Barium hydroxide octahydrate	$Ba(OH)_2 \times 8H_2O$			2.55×10^{-4}		
Barium iodate	$Ba(IO_3)_2$		1.5×10^{-9}	4.01×10^{-9}		
Barium iodate monohydrate	$Ba(IO_3)_2 \times H_2O$			1.67×10^{-9}		
Barium molybdate	$BaMoO_4$			3.54×10^{-8}		
Barium nitrate	$Ba(NO_3)_2$			4.64×10^{-3}		
barium oxalate	BaC_2O_4		2.3×10^{-8}		1.1×10^{-7}	1.6×10^{-7}
Barium phosphate	$Ba_3(PO_4)_2$				1.3×10^{-29}	3×10^{-23}

(*continues*)

TABLE 5-1 ***(continued)***

		K_{sp}^a (64–77°F)	K_{sp}^b (25°C)	K_{sp}^c (25°C)	K_{sp}^d (25°C)	K_{sp}^e (25°C)
Barium selenate	$BaSeO_4$			3.40×10^{-8}		
Barium sulfate	$BaSO_4$		1.1×10^{-10}	1.08×10^{-10}	1.1×10^{-10}	1.1×10^{-10}
Barium sulfite	$BaSO_3$		8×10^{-7}	5.0×10^{-10}	8.0×10^{-7}	
Barium thiosulfate	BaS_2O_3		1.6×10^{-5}			
Beryllium hydroxide	$Be(OH)_2$			6.92×10^{-22}		
Bismuthyl chloride	$BiOCl$		1.8×10^{-31}			
Bismuthyl hydroxide	$BiOOH$		4×10^{-10}			
Bismuth arsenate	$BiAsO_4$			4.43×10^{-10}		
Bismuth iodide	BiI			7.71×10^{-19}		
Cadmium arsenate	$Cd_3(AsO_4)_2$			2.2×10^{-33}		
Cadmium carbonate	$CdCO_3$		5.2×10^{-12}	1.0×10^{-12}		6.2×10^{-12}
Cadmium hydroxide	$Cd(OH)_2$		2.5×10^{-14}			
Cadmium iodate	$Cd(IO_3)_2$		2.3×10^{-8}	2.5×10^{-8}		
Cadmium fluoride	CdF_2			6.44×10^{-3}		
Cadmium hydroxide	$Cd(OH)_2$			7.2×10^{-15}		5.3×10^{-15}
Cadmium oxalate trihydrate	$CdC_2O_4 \times 3H_2O$			1.42×10^{-8}		
Cadmium phosphate	$Cd_3(PO_4)_2$			2.53×10^{-33}		
Caesium perchlorate	$CsClO_4$			3.95×10^{-3}		
Caesium periodate	$CsIO_4$			5.16×10^{-6}		
Calcium carbonate	$CaCO_3$		3.8×10^{-9}	3.36×10^{-9}	3.8×10^{-9}	5.0×10^{-9}
Calcium chromate	$CaCrO_4$		7.1×10^{-4}		7.1×10^{-4}	7.1×10^{-4}
Calcium fluoride	CaF_2		5.3×10^{-9}	3.45×10^{-11}	3.9×10^{-11}	1.5×10^{-10}
Calcium hydroxide	$Ca(OH)_2$		5.5×10^{-6}	5.02×10^{-6}	7.9×10^{-6}	4.7×10^{-6}
Calcium iodate	$Ca(IO_3)_2$		7.1×10^{-7}	6.47×10^{-6}		
Calcium iodate hexahydrate	$Ca(IO_3)_2 \times 6H_2O$			7.10×10^{-7}		
Calcium oxalate hydrate	$CaC_2O_4 \times H_2O$		1.96×10^{-8}	2.32×10^{-9}	2.3×10^{-9}	
Calcium hydrogen phosphate	$CaHPO_4$		1×10^{-7}			

Calcium molybdate	CaMoO		1.46×10^{-8}		
Calcium phosphate	$Ca_3(PO_4)_2$	1×10^{-26}	2.07×10^{-33}	1.0×10^{-25}	
Calcium sulfate	$CaSO_4$	9.1×10^{-6}	4.93×10^{-5}	2.4×10^{-5}	7.1×10^{-5}
Calcium sulfate dihydrate	$CaSO_4 \times 2H_2O$		3.14×10^{-5}		
Calcium sulfate hemihydrate	$CaSO_4 \times 0.5H_2O$		3.1×10^{-7}		
Calcium sulfide	CaS			8×10^{-6}	
Calcium sulfite	$CaSO_3$	6.8×10^{-8}		1.3×10^{-8}	
Chromium(II) hydroxide	$Cr(OH)_2$	2×10^{-16}			
Chromium(III) hydroxide	$Cr(OH)_3$	6.3×10^{-31}		6.7×10^{-31}	6.7×10^{-31}
Chromium phosphate	$CrPO_4$			2.4×10^{-23}	
Cobalt(II) arsenate	$Co_3(AsO_4)_2$		6.80×10^{-29}		
Cobalt(II) carbonate	$CoCO_3$	1.4×10^{-13}	1.0×10^{-10}	8.0×10^{-13}	1.0×10^{-10}
Cobalt(II) hydroxide (blue)	$Co(OH)_2$		5.92×10^{-15}	2.5×10^{-16}	1.1×10^{-15}
Cobalt(III) hydroxide	$Co(OH)_3$	1.6×10^{-44}			
Cobalt(II) iodate dihydrate	$Co(IO_3)_2 \times 2H_2O$		1.21×10^{-2}		
Cobalt(II) phosphate	$Co_3(PO_4)_2$		2.05×10^{-35}		
Cobalt (II) sulfide	CoS			5.9×10^{-21}	
Copper(I) bromide	CuBr		6.27×10^{-9}		6.3×10^{-9}
Copper(I) chloride	CuCl	1.2×10^{-6}	1.72×10^{-7}		1.7×10^{-7}
Copper(I) cyanide	CuCN	3.2×10^{-20}	3.47×10^{-20}		
Copper(I) iodide	CuI	1.1×10^{-12}	1.27×10^{-12}		1.1×10^{-12}
Copper(I) hydroxide	Cu_2OH		2×10^{-15}		
Copper(I) sulfide	Cu_2S	2.5×10^{-48}		7.9×10^{-37}	
Copper(I) thiocyanate	CuSCN		1.77×10^{-13}		
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.6×10^{-36}	7.95×10^{-36}		
Copper(II) carbonate	$CuCO_3$	1.4×10^{-10}		2.5×10^{-10}	2.5×10^{-10}
Copper(II) chromate	$CuCrO_4$	3.6×10^{-6}			
Copper(II) ferrocyanide	$Cu_2[Fe(CN)_6]$	1.3×10^{-16}			
Copper(II) hydroxide	$Cu(OH)_2$	2.2×10^{-20}	4.8×10^{-20}	1.6×10^{-19}	1.6×10^{-19}
Copper(II) iodate monohydrate	$Cu(IO_3)_2 \times H_2O$		6.94×10^{-8}		
Copper(II) oxalate	CuC_2O_4		4.43×10^{-10}		3×10^{-8}
Copper(II) phosphate	$Cu_3(PO_4)_2$		1.40×10^{-37}		

(*continues*)

TABLE 5-1 ***(continued)***

		$K_{sp}{}^a$ (64–77°F)	$K_{sp}{}^b$ (25°C)	$K_{sp}{}^c$ (25°C)	$K_{sp}{}^d$ (25°C)	$K_{sp}{}^e$ (25°C)
Copper(II) sulfide	CuS		6×10^{-37}	8×10^{-37}		
Copper(II) thiocyanate	$Cu(SCN)_2$		4.0×10^{-14}			
Europium(III) hydroxide	$Eu(OH)_3$			9.38×10^{-27}		
Gallium(III) hydroxide	$Ga(OH)_3$			7.28×10^{-36}		
Fluorapatite	$Ca_5(PO_4)_3F$		1.0×10^{-60}			
Hydroxyapatite	$Ca_5(PO_4)_3OH$		1.0×10^{-36}			
Iron(II) carbonate	$FeCO_3$		3.2×10^{-11}	3.13×10^{-11}	3.5×10^{-11}	2.1×10^{-11}
Iron(II) fluoride	FeF_2			2.36×10^{-6}		
Iron(II) hydroxide	$Fe(OH)_2$		8.0×10^{-16}	4.87×10^{-17}	7.9×10^{-15}	4.9×10^{-17}
Iron(III) arsenate	$FeAsO_4$		5.7×10^{-21}			
Iron(III) ferrocyanide	$Fe_4[Fe(CN)_6]_3$		3.3×10^{-41}			
Iron(III) hydroxide	$Fe(OH)_3$		4×10^{-38}	2.79×10^{-39}	6.3×10^{-38}	2.6×10^{-39}
Iron(III) phosphate	$FePO_4$		1.3×10^{-22}			
Iron(III) phosphate dihydrate	$FePO_4 \times 2H_2O$			9.91×10^{-16}		
Iron (III) sulfide	Fe_2S_3				1.4×10^{-88}	
Lead(II) arsenate	$Pb_3(AsO_4)_2$		4.0×10^{-36}			
Lead(II) azide	$Pb(N_3)_2$		2.5×10^{-9}			
Lead(II) bromate	$Pb(BrO_3)_2$		7.9×10^{-6}			
Lead(II) bromide	$PbBr_2$		4.0×10^{-5}	6.60×10^{-6}	6.3×10^{-6}	6.6×10^{-6}
Lead(II) carbonate	$PbCO_3$		7.4×10^{-14}	7.40×10^{-14}	1.5×10^{-13}	7.4×10^{-14}
Lead(II) chloride	$PbCl_2$		1.6×10^{-5}	1.70×10^{-5}	1.7×10^{-5}	1.2×10^{-5}
Lead(II) chromate	$PbCrO_4$		2.8×10^{-13}	3×10^{-13}	1.8×10^{-14}	2.8×10^{-13}
Lead(II) fluoride	PbF_2		2.7×10^{-8}	3.3×10^{-8}	3.7×10^{-8}	
Lead(II) hydroxide	$Pb(OH)_2$		1.2×10^{-5}	1.43×10^{-20}	2.8×10^{-16}	1.2×10^{-15}
Lead(II) iodate	$Pb(IO_3)_2$		2.6×10^{-13}	3.69×10^{-13}		
Lead(II) iodide	PbI_2		7.1×10^{-9}	9.8×10^{-9}	8.7×10^{-9}	8.5×10^{-9}
Lead(II) oxalate	PbC_2O_4			8.5×10^{-9}		4.8×10^{-12}
Lead (II) phosphate	$Pb_3(PO_4)_2$				3.0×10^{-44}	7.9×10^{-43}

Lead(II) selenate	$PbSeO_4$		1.37×10^{-7}		
Lead(II) sulfate	$PbSO_4$	1.6×10^{-8}	2.53×10^{-8}	1.8×10^{-8}	1.8×10^{-8}
Lead (II) sulfide	PbS			3.2×10^{-28}	
Lithium carbonate	Li_2CO_3	2.5×10^{-2}	8.15×10^{-4}		
Lithium fluoride	LiF	3.8×10^{-3}	1.84×10^{-3}		
Lithium phosphate	Li_3PO_4	3.2×10^{-9}	2.37×10^{-4}		
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}	3×10^{-13}		
Magnesium arsenate	$Mg_3(AsO_4)_2$	2.1×10^{-20}			
Magnesium carbonate	$MgCO_3$	3.5×10^{-8}	6.82×10^{-6}	4.0×10^{-5}	6.8×10^{-6}
Magnesium carbonate trihydrate	$MgCO_3 \times 3H_2O$		2.38×10^{-6}		
Magnesium floride	MgF_2				7.4×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$		4.37×10^{-7}		
Manganese(II) oxalate dihydrate	$MnC_2O_4 \times 2H_2O$		1.70×10^{-7}		
Magnesium carbonate pentahydrate	$MgCO_3 \times 5H_2O$		3.79×10^{-6}		
Magnesium fluoride	MgF_2	3.7×10^{-8}	5.16×10^{-11}	6.4×10^{-9}	
Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}	5.61×10^{-12}	1.5×10^{-11}	5.6×10^{-12}
Magnesium oxalate	MgC_2O_4	7×10^{-7}		8.6×10^{-5}	4.8×10^{-6}
Magnesium oxalate dihydrate	$MgC_2O_4 \times 2H_2O$		4.83×10^{-6}		
Magnesium phosphate	$Mg_3(PO_4)_2$	1×10^{-25}	1.04×10^{-24}		
Manganese(II) carbonate	$MnCO_3$	1.8×10^{-11}	2.24×10^{-11}	1.8×10^{-11}	2.2×10^{-11}
Manganese(II) hydroxide	$Mn(OH)_2$	1.9×10^{-9}	2×10^{-13}	4.6×10^{-14}	2.1×10^{-13}
Manganese(II) sulfide	MnS	2.5×10^{-13}	3×10^{-14}	5.1×10^{-15}	
Mercury(I) bromide	Hg_2Br_2	5.6×10^{-23}	6.40×10^{-23}		6.4×10^{-23}
Mercury(I) carbonate	Hg_2CO_3		3.6×10^{-17}		
Mercury(I) chloride	Hg_2Cl_2	5.0×10^{-13}	1.43×10^{-18}		1.4×10^{-18}
Mercury(I) chromate	Hg_2CrO_4	2.0×10^{-9}			2.0×10^{-9}
Mercury(I) cyanide	$Hg_2(CN)_2$	5×10^{-40}			
Mercury(I) iodide	HgI_2	4.5×10^{-29}	5.2×10^{-29}		4.5×10^{-29}
Mercury(I) fluoride	Hg_2F_2		3.10×10^{-6}		
Mercury(I) oxalate	$Hg_2C_2O_4$		1.75×10^{-13}		1.8×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	7.4×10^{-7}	6.5×10^{-7}		6.8×10^{-7}

(continues)

TABLE 5-1 ***(continued)***

		$K_{sp}{}^{a}$ (64–77°F)	$K_{sp}{}^{b}$ (25°C)	$K_{sp}{}^{c}$ (25°C)	$K_{sp}{}^{d}$ (25°C)	$K_{sp}{}^{e}$ (25°C)
Mercury(I) sulfide	Hg_2S		1.0×10^{-47}			
Mercury(I) thiocyanate	$Hg2(SCN)_2$		3.0×10^{-20}	3.2×10^{-20}		
Mercury(II) bromide	$HgBr_2$			6.2×10^{-20}		
Mercury(II) hydroxide	$Hg(OH)_2$			3.6×10^{-26}		3.1×10^{-26}
Mercury(II) iodide	HgI_2			2.9×10^{-29}		
Mercury(II) sulfide	HgS		1.6×10^{-52}	2×10^{-53}		
Mercury(II) thiocyanate	$Hg(SCN)_2$		2.8×10^{-20}			
Neodymium carbonate	$Nd_2(CO_3)_3$			1.08×10^{-33}		
Nickel(II) carbonate	$NiCO_3$		6.6×10^{-9}	1.42×10^{-7}	6.6×10^{-9}	1.3×10^{-7}
Nickle cyanide	$Ni(Cn)_2$				3.0×10^{-23}	
Nickel(II) hydroxide	$Ni(OH)_2$		2.0×10^{-15}	5.48×10^{-16}	2.8×10^{-16}	5.5×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$			4.71×10^{-5}		
Nickel(II) phosphate	$Ni_3(PO_4)_2$			4.74×10^{-32}		
Nickle(II) sulfide	NiS				3.0×10^{-21}	
Palladium(II) thiocyanate	$Pd(SCN)_2$			4.39×10^{-23}		
Potassium hexachloroplatinate	K_2PtCl_6			7.48×10^{-6}		
Potassium perchlorate	$KClO_4$			1.05×10^{-2}		
Potassium periodate	KIO_4			3.71×10^{-4}		
Praseodymium hydroxide	$Pr(OH)_3$			3.39×10^{-24}		
Radium iodate	$Ra(IO_3)_2$			1.16×10^{-9}		
Radium sulfate	$RaSO_4$			3.66×10^{-11}		
Rubidium perchlorate	$RuClO_4$			3.00×10^{-3}		
Scandium fluoride	ScF_3		4.2×10^{-18}	5.81×10^{-24}		
Scandium hydroxide	$Sc(OH)_3$		4.2×10^{-18}	2.22×10^{-31}		
Silver arsenate	Ag_3AsO_4		1.0×10^{-22}	1.03×10^{-22}		
Silver acetate	$AgC_2H_3O_2$		2.0×10^{-3}	1.94×10^{-3}		4.4×10^{-3}
Silver azide	AgN_3		2.0×10^{-8}			
Silver benzoate	$AgC_7H_5O_2$		2.5×10^{-5}			

Silver bromate	$AgBrO_3$	5.5×10^{-5}	5.38×10^{-5}		
Silver bromide	$AgBr$	5.3×10^{-13}	5.35×10^{-13}	3.3×10^{-13}	5.4×10^{-13}
Silver carbonate	Ag_2CO_3	8.1×10^{-12}	8.46×10^{-12}		8.1×10^{-12}
Silver chloride	$AgCl$	1.8×10^{-10}	1.77×10^{-10}	1.8×10^{-10}	1.8×10^{-10}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}	1.12×10^{-12}	9.0×10^{-12}	2.0×10^{-12}
Silver cyanide	$AgCN$	1.2×10^{-16}	5.97×10^{-17}	1.2×10^{-16}	
Silver hydroxide	$AgOH$			2.0×10^{-8}	
Silver iodate	$AgIO_3$	3.0×10^{-8}	3.17×10^{-8}		
Silver iodide	AgI	8.3×10^{-17}	8.52×10^{-17}	1.5×10^{-16}	8.5×10^{-17}
Silver nitrite	$AgNO_2$	6.0×10^{-4}			
Silver oxalate	$Ag_2C_2O_4$	3.6×10^{-11}	5.40×10^{-12}	8.1×10^{-12}	3.5×10^{-11}
Silver(I) phosphate	Ag_3PO_4		8.89×10^{-17}	1.3×10^{-20}	8.9×10^{-17}
Silver sulfate	Ag_2SO_4	1.4×10^{-5}	1.20×10^{-5}	1.7×10^{-5}	1.2×10^{-5}
Silver sulfite	$AgSO_3$	1.5×10^{-14}	1.50×10^{-14}	1.5×10^{-14}	
Silver thiocyanate	$AgSCN$	1.0×10^{-12}	1.03×10^{-12}		
Strontium arsenate	$Sr_3(AsO_4)_2$		4.29×10^{-19}		
Strontium carbonate	$SrCO_3$	1.1×10^{-10}	5.60×10^{-10}		5.6×10^{-10}
Strontium chromate	$SrCrO_4$	2.2×10^{-5}			2.2×10^{-5}
Strontium fluoride	SrF_2	2.5×10^{-9}	4.33×10^{-9}		2.5×10^{-9}
Strontium hydroxide	$Sr(OH)_2$				6.4×10^{-3}
Strontium iodate	$Sr(IO_3)_2$		1.14×10^{-7}		
Strontium iodate monohydrate	$Sr(IO_3)_2 \times H_2O$		3.77×10^{-7}		
Strontium iodate hexahydrate	$Sr(IO_3)_2 \times 6H_2O$		4.55×10^{-7}		
Strontium oxalate	SrC_2O_4	4×10^{-7}	5×10^{-8}		5×10^{-8}
Strontium sulfate	$SrSO_4$	3.2×10^{-7}	3.44×10^{-7}		3.5×10^{-7}
Strontium sulfite	$SrSO_3$	4×10^{-8}			
Thallium(I) bromate	$TlBrO_3$	1.7×10^{-4}	1.10×10^{-4}		
Thallium(I) bromide	$TlBr$	3.4×10^{-6}	3.71×10^{-6}		
Thallium(I) chloride	$TlCl$	1.7×10^{-4}	1.86×10^{-4}		
Thallium(I) chromate	Tl_2CrO_4	9.8×10^{-15}	8.67×10^{-13}		
Thallium(I) hydroxide	$Tl(OH)_3$		1.68×10^{-44}		
Thallium(I) iodate	$TlIO_3$	3.1×10^{-6}	3.12×10^{-6}		

(*continues*)

TABLE 5-1 ***(continued)***

		$K_{sp}{}^{a}$ (64–77°F)	$K_{sp}{}^{b}$ (25°C)	$K_{sp}{}^{c}$ (25°C)	$K_{sp}{}^{d}$ (25°C)	$K_{sp}{}^{e}$ (25°C)
Thallium(I) iodide	TlI		6.5×10^{-8}	5.54×10^{-8}		
Thallium(I) sulfide	Tl_2S		6×10^{-22}	6×10^{-22}		
Thallium(I) thiocyante	$TlSCN$		1.6×10^{-4}	1.57×10^{-4}		
Thallium(III) hydroxide	$Tl(OH)_3$		6.3×10^{-46}			
Tin(II) hydroxide	$Sn(OH)_2$		1.4×10^{-28}	5.45×10^{-27}		
Tin(II) sulfide	SnS		1×10^{-26}			
Yttrium carbonate	$Y_2(CO_3)_3$			1.03×10^{-31}		
Yttrium fluoride	YF_3			8.62×10^{-21}		
Yttrium hydroxide	$Y(OH)_3$			1.00×10^{-22}		
Yttrium iodate	$Y(IO_3)_3$			1.12×10^{-10}		
Zinc arsenate	$Zn_3(AsO_4)_2$			2.8×10^{-28}		
Zinc carbonate	$ZnCO_3$		1.4×10^{-11}	1.46×10^{-10}	1.5×10^{-11}	1.2×10^{-10}
Zinc carbonate monohydrate	$ZnCO_3 \times H_2O$			5.42×10^{-11}		
Zinc cyanide	$Zn(CN)_2$		3×10^{-16}		8.0×10^{-12}	
Zinc fluoride	ZnF			3.04×10^{-2}		
Zinc hydroxide	$Zn(OH)_2$		1.2×10^{-17}	3×10^{-17}	4.5×10^{-17}	4.1×10^{-17}
Zinc iodate	$Zn(IO_3)_2$		3.9×10^{-6}			
Zinc iodate dihydrate	$Zn(IO_3)_2 \times 2H_2O$			4.1×10^{-6}		
Zinc oxalate dihydrate	$ZnC_2O_4 \times 2H_2O$			1.38×10^{-9}		
Zinc oxalate	ZnC_2O_4		2.7×10^{-8}			1.4×10^{-9}
Zinc phosphate	$Zn_3(PO_4)_2$		9.0×10^{-33}		9.1×10^{-33}	
Zinc selenide	$ZnSe$			3.6×10^{-26}		
Zinc selenite monohydrate	$ZnSe \times H_2O$			1.59×10^{-7}		

[a] EPA Summary Report, Control and Treatment Technology for the Metal Finishing Industry: Sulfide Precipitation, April 1980.

[b] California State University—Dominguez Hills, Selected Solubility Products and Formation Constants at 25°C, http://www.csudh.edu/oliver/chemdata/data-ksp.htm

[c] Solubility Product Constants, http://www.ktf-split.hr/periodni/en/abc/kpt.html

[d] Table of Solubility Product Constants (K_{sp} @ 25°C), http://chemistry.uah.edu/CourseWare/ch123/resources/ch123solubilityconstants.html

[e] Solubility Product Constant (K_{sp}) Values at 25°C, http://users.stlcc.edu/gkrishnan/ksptable.html

Often, concentrations are expressed in units of mg/L rather than moles per liter. The conversion of a concentration from mg/L to moles per liter is done by dividing the concentration in mg/L by the molecular weight of the compound. This conversion is represented by the following formula:

$$[\mathrm{Me}^+] = (\mathrm{Me}^+)/(\mathrm{MW} * 1{,}000\,\mathrm{mg/g})$$

where

$[\mathrm{Me}^+]$ = the concentration of a metal cation in solution in moles per liter
(Me^+) = the concentration of the metal cation in solution in mg/L
MW = the molecular weight of the metal in g/mole.

When considering the precipitation of heavy metals, we typically increase the concentration of the anionic species in solution so that solubility product of the metal concentration times the anion concentration is exceeded, and the result is the precipitation of the metal. The theoretical concentration of the anionic species required to achieve the desired metal concentration can be calculated by rearranging the above formula as follows:

$$[\mathrm{An}^-] = [\mathrm{Me}^+{}_{\mathrm{final}}]/K_{\mathrm{sp}}$$

where

$[\mathrm{Me}^+{}_{\mathrm{final}}]$ = the desired final concentration of a metal cation in solution in moles per liter

It should be noted that this simple analysis evaluates equilibrium conditions and does not consider the feasibility of the reaction from thermodynamic or kinetic (rate of reaction) perspectives. It does establish conceptual approaches for the removal of the metal. These approaches should be evaluated further using more specific geochemical models that account for these effects. The total stoichiometric anion demand also needs to consider removal of not just the target metal, but also other cations that will compete for and precipitate with the added anion. This can be accomplished through a cation–anion balance. Ultimately, the actual required concentration of an anionic species required to achieve the desired concentration of the metal and confirmation of the thermodynamic and kinetic feasibility of the reactions in an aboveground reactor are best determined through a program of bench-scale or pilot-scale testing. Bench-scale testing is described further below.

Many metals can be removed as metal hydroxide precipitates. The pH will normally have to be raised above 7 to remove the metals in this manner. Figure 5-1 summarizes the solubilities of the various heavy metals as a hydroxide precipitate. For metals precipitation, lime (calcium oxide) or caustic (sodium hydroxide) are necessary to reach required pH ranges. The main differences between the two compounds are that lime is less expensive but more difficult to use. Lime costs about 40 to 60 percent less than caustic. Actual prices will depend heavily on transportation costs. Specific prices should be obtained

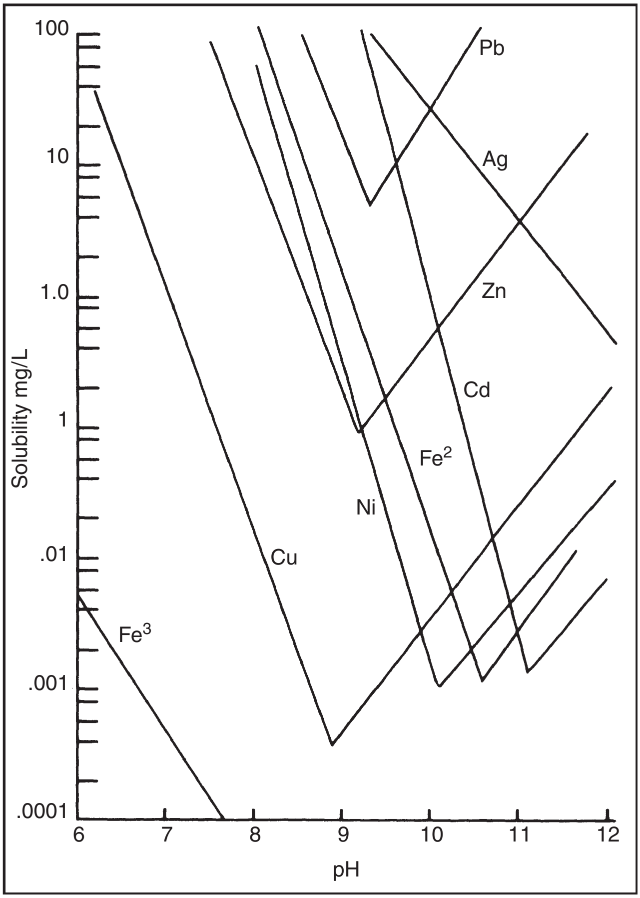

FIGURE 5-1. Solubilities of metal hydroxides at various pHs. (Courtesy of Graver Water.)

for each project. Lime is normally fed as a hydrated lime slurry. The material is stored dry and slurried before mixing with the acidic groundwater. Lines can become clogged easily, and great care should be taken to keep the slurry in motion.

Not all metals will precipitate upon an increase in pH. If the metals are being kept in solution by a chelant, the metals will not follow the solubility curves in Figure 5-1. In addition, iron in the ferrous state and chromium in the hexavalent state will not precipitate at high pH. Arsenic is another inorganic compound that will not precipitate by a simple increase in pH. All of these compounds require chemical addition for precipitation.

Another way to remove metals from solution is to precipitate them as a sulfide precipitate rather than a hydroxide precipitate. The solubility is still dependent on the pH, but, in general, a metal sulfide is less soluble than a metal hydroxide. Because the solubility is less, the metal will precipitate out of the water, resulting in the water effluent metal concentration being less. Also, in the case of metals like lead and zinc, the range of pHs at which the reaction can be run is increased. Figure 5-2 summarizes the solubility of metal sulfide compounds. The design engineer may want to consider this technology for long-term projects if there is a reason that very low metal concentrations are required in the effluent from the treatment system.

Iron is not a toxic metal. However, it can cause problems with processes, pipes, equipment, and final use of the water. As presented in the air-stripping section of Chapter 2, iron is a nuisance metal that has to be considered in the design of a treatment system for VOC removal. Iron is found in many groundwaters naturally. The technology for removing iron is well established. Soluble ferrous iron has to be oxidized to the insoluble ferric state. In the ferric state, iron is not soluble above a pH of 7. Oxidation occurs readily at pH 7.0 to 7.5. The water must simply be aerated within this pH range, and ferrous iron will convert to ferric iron. Diffused air aerators are one means of providing oxygen to the water. The amounts of air used vary from 0.04 to 1.5 cubic meters per cubic meter (m^3/m^3) of water.[2] A reaction time of up to 30 minutes should be allowed.

The addition of sodium or calcium hypochlorite could also be used to oxidize iron from the ferrous to the ferric state. These compounds are available in liquid form, generally within the 12- to 15-percent concentration range. They degrade with time and therefore cannot be stored for long times. Generally, no more than one month's storage is practical. The problem with using these chemicals is that you are introducing chlorine to the waste stream; this has the potential to

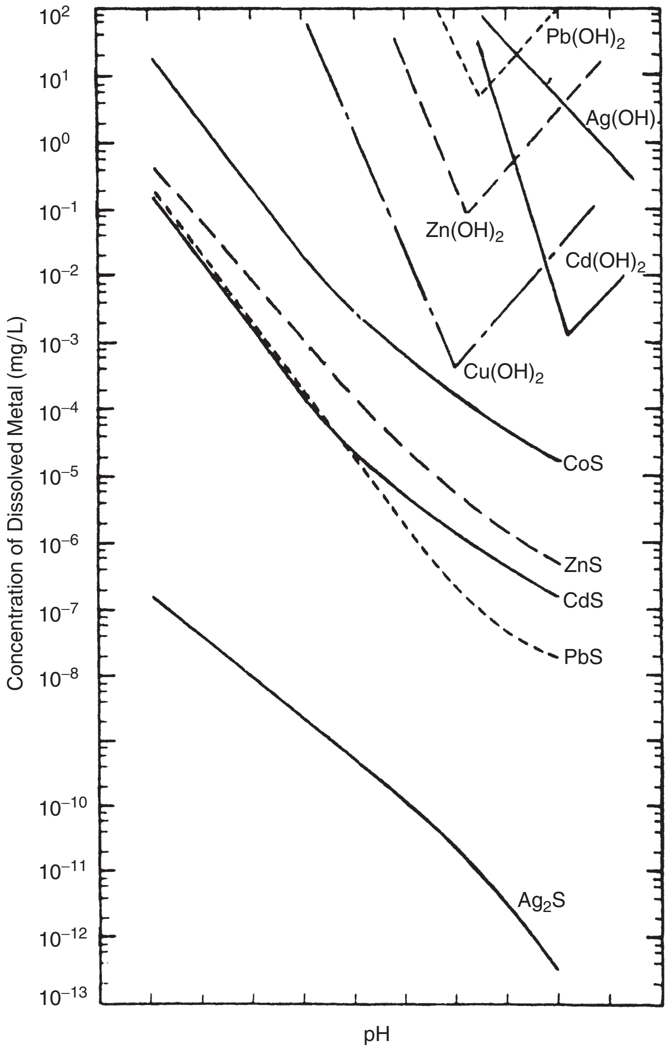

FIGURE 5-2. Solubilities of metal sulfides and metal hydroxides at various pHs. (Courtesy of Graver Water.)

form trichloromethanes and other chlorinated compounds. Therefore, their use should be considered only when air emissions are a serious concern and low levels of trichloromethanes or trihalomethanes are acceptable to discharge. Hydrogen peroxide can also be used as a chemical oxidant for iron. It is more expensive than sodium or calcium hypochlorite, but it has a longer shelf life and does not cause the problem of creating chlorinated hydrocarbons.

Barium is a widely distributed metal that is present in the earth's crust, igneous rocks, sandstones, and shales as the insoluble compound barite ($BaSO_4$). In this insoluble form, barium is considered nontoxic. According to Conner,[3] barite is mined and chemically processed to produce soluble forms such as the following:

- Barium borate (BaB_2O_4), which is used in paint pigments
- Barium carbonate ($BaCO_3$), which is used in brick manufacturing and oil-well drilling muds
- Barium chloride ($BaCl_2$), which is used in pigments, metal-case hardening, and heat-treating baths
- Barium hydroxide [$Ba(OH)_2$], which is used in paper and plastics manufacturing as a dispersant for pigments and in self-extinguishing polyurethane foams
- Barium nitrate ($BaNO_3$), which is used in pyrotechnics and explosives

When found in the soluble form, barium is easily reacted with sulfate salts, such as sodium or calcium sulfate, to form relatively insoluble barium sulfate. The reaction is described below:

$$Ba^{2+} + SO_4{}^{2-} \rightarrow BaSO_4\,(s)$$

Barium sulfate has a solubility of 1.4 mg/L as barium[3] The treatment of leachable barium in sludges and soils has been successfully accomplished by mixing the sludge or soil with solid-phase gypsum (calcium sulfate).

Hexavalent chromium is a toxic heavy metal. Hexavalent chromium is used only in industrial plants and is not found naturally in groundwater. Like ferrous iron, it is soluble in water at high pH. Methods for treating hexavalent chromium have been developed for industrial wastewater. The hexavalent chromium must be reduced to the trivalent state for removal. Trivalent chromium is not soluble at high pH (see Figure 5-1). The standard reduction treatment technique is to lower the pH of the water to 2 or 3. Next, a chemical reducing agent is added to the water. The most common reducing agent is sulfur dioxide, but sodium bisulfite, metabisulfite, hydrosulfite, or ferrous sulfate are also used. The pH is then raised, and the trivalent chromium precipitates.

Hexavalent chromium reduces readily but not at a fast rate. The longer that the hexavalent chromium is in the groundwater and the more contact it has with other material and water, the more likely it will naturally be reduced to the trivalent state. However, when hexavalent chromium is found in the groundwater to be treated, at least a 20- to 30-minute residence time should be used for the reduction reaction in the treatment system. As with all inorganic treatment methods, the reaction time for hexavalent chromium reaction should be established by laboratory tests.

Available treatment technologies for mercury removal include precipitation/coprecipitation, coagulation with filtration, lime softening, GAC adsorption, ion exchange, membrane filtration, and biological treatment.[4] Mercury precipitation as a hydroxide is ineffective because mercury hydroxide is soluble over a wide pH range. Sulfide addition to precipitate highly insoluble mercury sulfide is the most common precipitation treatment reported.[5] It has been reported by Patterson[5] that the lower treatability limit for mercury is 10 to 20 mg/L with sulfide precipitation, 1 to 5 mg/L with ion exchange, 1 to 10 mg/L with alum coagulation, 0.5 to 5 mg/L with iron coagulation, and 0.25 to 20 mg/L with activated carbon, depending on initial concentration. More recently, combinations of these technologies have been successfully used to achieve effluent concentrations below 2 μg/L.[4] Nanotechnology using thiol-functional groups that adsorb heavy metals represents a promising technology that is currently under development. An adsorbent called Thiol-SAMMS (i.e., Thiol-Self Assembled Monolayers on Mesoporous Silica) has been developed and tested at the Pacific Northwest National Laboratory.[4] Thiol-functional groups have demonstrated a high capacity to adsorb heavy metals, including mercury, and removal efficiencies greater than 99 percent have been achieved with this developing technology.

One final inorganic that is typically removed by chemical addition is arsenic. Arsenic in the groundwater may be either in the arsenite ion or the arsenate ion form. Because the presence of dissolved oxygen will oxidize arsenite to arsenate, the majority of groundwater contamination cases involve the arsenate form. If a deep aquifer is contaminated, the groundwater may have to be oxidized prior to arsenic treatment because the arsenate form is more easily removed than the arsenite form. Arsenic requires the formation of a floc for removal from the water. Increasing the pH with lime will remove some of the arsenic. The same increase in pH with caustic soda will not remove the arsenic because of the lower amount of solids formed. Arsenic treatment processes for both municipal wastes and industrial wastes, according to available literature, are similar and commonly involve coprecipitation by addition of a polyvalent metallic coagulant to produce a hydroxide floc.[5] It has been the author's experience that the most efficient way to remove arsenic is to add iron, in the ferrous or ferric state, at a pH between 5 and 6, and then to increase the pH to 8 or 9 with lime. Iron/arsenic ratios should be around 8:1. Using iron/arsenic in combinations above or below that ratio will decrease the removal efficiency.

Each of these precipitation reactions can be tested in the laboratory using a simple method called a jar test. A typical jar test is performed using an apparatus that permits mixing up to six jars simultaneously (Figure 5-3). Site groundwater is amended with the chemical to cause the precipitation of the metal over a range of concentrations. The jars are first rapidly mixed for a set period, typically 30 seconds to 2 minutes, to distribute the chemical. This is followed by a period of slow, gentle mixing for 10 to 30 minutes to allow floc formation. The jars are observed for floc generation, size, and settleability. At the conclusion of the test, after the floc is allowed to settle, the resulting supernatant can be sampled and analyzed to determine if the desired precipitation of the metal occurred. These types of jar tests provide insight into not only the concentration of chemicals required to achieve the precipitation of the metal but also the reaction time, mixing, flocculation, and settling characteristics of the precipitate so those factors can be accounted for in the final design.

Before we leave this section, one further method of precipitation should be reviewed. Iron can be added to the water by electrochemical

FIGURE 5-3. PB-700 Series Six-Paddle Standard JarTester. (Phipps & Bird.)

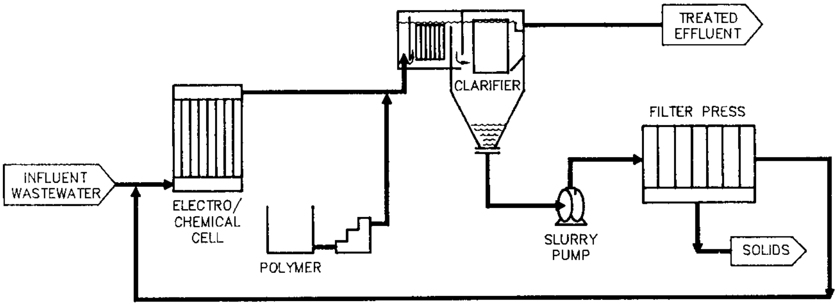

FIGURE 5-4. Process flow diagram of electromechanical precipitation. (Courtesy of Andco.)

methods to enhance the precipitation of other inorganics. Electrochemical technology for the treatment of heavy metals is a relatively new technology, since the early 1970s. The system uses sacrificial electrodes to produce an insoluble ferrous ion, which adsorbs and coprecipitates heavy metals. The mechanism is not fully understood, but it is believed to be primarily an adsorption process, with the metals being adsorbed onto the iron hydroxide matrix that is formed in the electrochemical cell, as shown in Figure 5-4.

The electrochemical process can be operated at neutral pH, which may eliminate the additional pH adjustment step for metal treatment. Equipment required for a typical electrochemical process is in Figure 5-5. In the process of producing the ferrous ion, the electrodes are consumed and will require replacement. To keep the electrodes clean, a diluted acid wash is used approximately once a day. Most of the maintenance can be set up to function on an automatic basis. There is a large amount of field experience on treating industrial waste, but this technology has only recently been applied to groundwater treatment. However, the ability to design the technology for small flows and have automatic operation makes it a good technology for groundwater treatment.

REMOVAL OF SUSPENDED SOLIDS

Flocculation

By chemical addition and pH adjustment, the inorganic contaminants are converted to a nonsoluble form. All the waste is now contained in suspended solids that must be removed from the water. These suspended solids are all heavier than water. However, these solids will

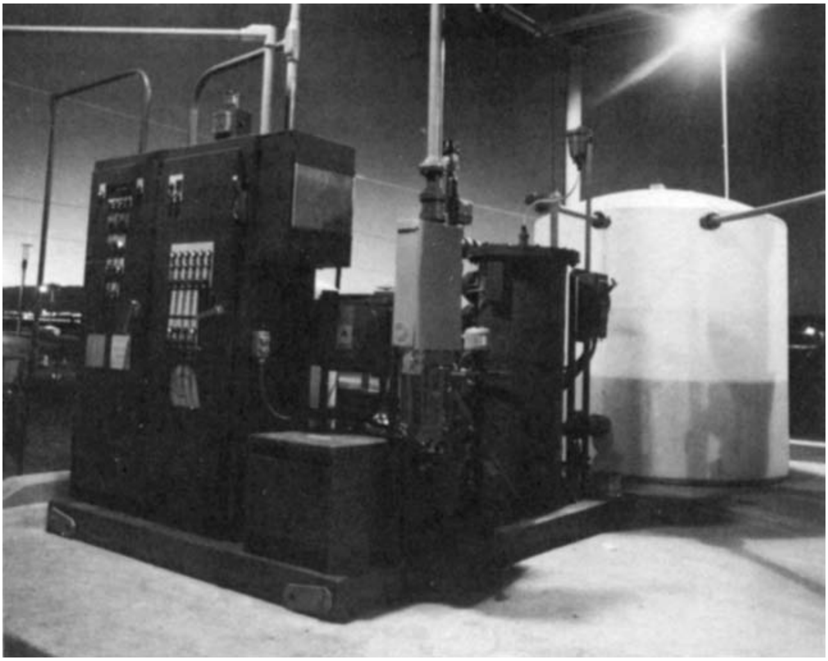

FIGURE 5-5. Electromechanical treatment system. (Courtesy of Andco.)

not be effectively removed simply by placing the groundwater in a quiescent tank and allowing the particles to settle.

There are four types of gravitational particle settling: discrete particle settling, flocculent settling, hindered (zone) settling, and compression settling. Other types of gravitational settling include high-rate clarification, accelerated gravity settling, and flotation.[6]

Discrete particle settling occurs when particles act as individuals, without interactions with other particles, and are allowed to settle by gravity. Flocculent settling is a process in which settling particles join together (flocculate), resulting in particles with a larger mass. Particles with a larger mass will settle faster. Zone settling occurs when forces between particles are strong enough to prevent settling. These forces result in zones of particles that settle as a unit. Compression settling is when solids concentrations are sufficient enough that settling occurs as a result of the compression caused by adding additional solids.

Settling of discrete, nonfloculating particles is described by the classic laws of sedimentation formulated by Newton and Stokes. Newton's law demonstrates the balance between the gravitational force of the particle and drag force of the particle in determining the terminal settling velocity.[6]

Gravitational force:

$$F_{\mathrm{g}} = (\rho_{\mathrm{p}} - \rho_{\mathrm{w}}) g V_{\mathrm{p}}$$

where

F_{g} = gravitational force, MLT^{-2} ($\mathrm{kg \cdot m/s^2}$)
ρ_{p} = density of particle, ML^{-3} ($\mathrm{kg/m^3}$)
ρ_{w} = density of water, ML^{-3} ($\mathrm{kg/m^3}$)
g = acceleration due to gravity, LT^{-2} ($9.81\,\mathrm{m/s^2}$)
V_{p} = volume of particle, L^3 (m^3)

Drag force:

$$F_{\mathrm{d}} = \frac{C_{\mathrm{d}} A_{\mathrm{p}} \rho_{\mathrm{w}} \nu_p^2}{2}$$

where

F_{d} = frictional drag force, MLT^{-2} ($\mathrm{kg \cdot m/s^2}$)
C_{d} = drag coefficient (unitless)
A_{p} = cross-sectional or projected area of particle in direction of flow, L^2 (m^2)
ν_{p} = particle settling velocity, LT^{-1} (m/s)

Equating the gravitational force and the drag force and solving for the velocity of the particle yields the equation for the terminal velocity of the settling particle.[6]

Terminal velocity of particle:

$$\nu_{\mathrm{p(t)}} = \sqrt{\frac{4g}{3C_{\mathrm{d}}} \left(\frac{\rho_{\mathrm{p}} - \rho_{\mathrm{w}}}{\rho_{\mathrm{w}}} \right) d_{\mathrm{p}}} \approx \sqrt{\frac{4g}{3C_{\mathrm{d}}} \left(sg_{\mathrm{p}} - 1 \right) d_{\mathrm{p}}}$$

where

$\nu_{\mathrm{p(t)}}$ = particle terminal settling velocity, LT^{-1} (m/s)
d_{p} = diameter of particle, L (m)
sg_{p} = specific gravity of particle

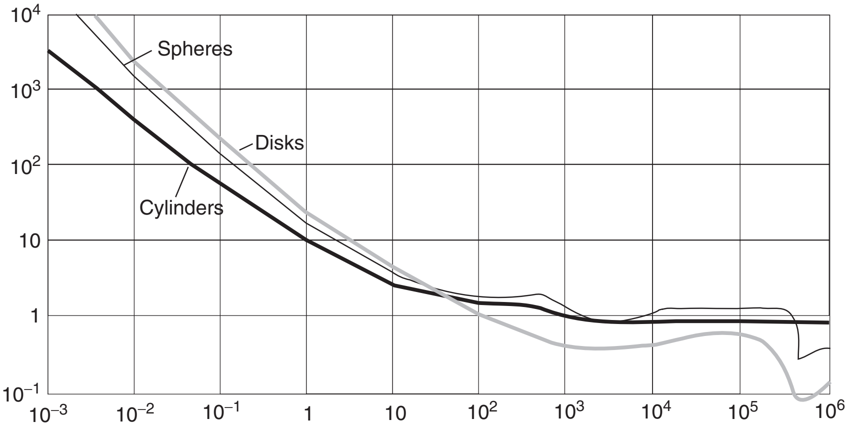

FIGURE 5-6. Coefficient of drag as a function of Reynolds number. (*Source*: Adapted from Metcalf & Eddy, *Wastewater Treatment*, 4th edition, McGraw-Hill, New York, 2003.)

The drag coefficient is variable depending on whether the surrounding flow is laminar or turbulent and on the shape of the particle (Figure 5-6). All the above equations assume a spherical particle.[6]

For nonspherical particles, the above equations require a shape factor be inserted. This is necessary because, in most cases, the settling particles are not spherical. The Reynolds number can be calculated using the following formula:

$$N_R = \frac{v_p d_p \rho_w}{\mu} \approx \frac{v_p d_p}{\nu}$$

where

μ = dynamic viscosity, $\mathrm{MTL^{-2}}$ ($\mathrm{N{\cdot}s/m^2}$)
ν = kinematic viscosity, $\mathrm{L^2T^{-1}}$ ($\mathrm{m^2/s}$)

For nonspherical particles, the equation becomes:

$$\approx \sqrt{\frac{4g}{3C_d\phi}\left(sg_p - 1\right) d_p}$$

where

ϕ = is a shape factor. The value of shape factor is 1.0 for spheres, 2.0 for sand grains, and up to and greater than 20 for fractal floc.[6]

Stoke's law can be used for settling in the laminar region. The laminar region is defined by an area with a Reynolds number less than 1.0. Stoke's law is as follows (assumes spherical particles)[6]:

$$v_p = \frac{g(\rho_p - \rho_w)d_p^2}{18\mu} \approx \frac{g(sg_p - 1)d_p^2}{18\nu}$$

$$F_d = 3\pi v_p d_p$$

For example, assume that all of the particles have a specific gravity of 2.65 settling in water with a temperature of 30°C (kinematic viscosity of $1.003 * 10^{-6}$ $\mathrm{m^2/s}$). The particles are assumed to be spheres. Calculation of the settling velocity using Stoke's law indicates laminar flow is present. The particles that have a diameter of 0.1 millimeters (mm), about the size of fine sand, will take 33 seconds to settle 1 foot. Particles with a 0.01-mm diameter, about the size of silt, will take 56 minutes to settle the same 1 foot. Finally, particles with a diameter of 0.001 mm, about the size of bacteria, will take 94 hours to settle 1 foot. Colloidal particles would take years to settle the same distance.

The sizes of the particles generated by the chemical addition and pH adjustment will range from colloidal to fine sand. The specific gravity will be lower than 2.65 and will vary depending on the metal precipitated and the chemicals used. As can be seen, a simple tank will not remove all of the suspended solids. The small particles must be brought together before they will settle from the water. This process is called flocculation.

There are two basic steps to flocculation. First, the particles all have the same charge on their surfaces, usually a negative charge. This charge is what keeps the particles separate. The first step is to neutralize this charge so that the particles can come into contact. When the particles are in contact, they will not separate unless subjected to high shear forces.

When the charge is neutralized, the second step is to agglomerate more and more particles together. The particles require gentle mixing so that they come into contact with other particles but not with so much force that the particles are broken apart. Floc is the precipitate that forms when the particles agglomerate. Flocculated solids should never be run through a centrifugal pump. The shear forces in the pump would easily tear apart the fragile floc.

The best way to increase the size of the particles depends on the concentration of the suspended solids. The higher the concentration, the more contact will occur between the particles. At low concentrations, the particles are so far apart that the gentle mixing would have to continue for a very long period of time for all of the particles to contact the other particles.

One method to improve the efficiency of flocculation is to introduce coagulants. When the pH is raised with lime, both pH adjustment and coagulation occur. Coagulants enhance the formation of floc. Typical coagulants among the hydrolyzing metal ions are aluminum sulfate (alum), ferrous sulfate (copperas), and ferric chloride. Alum is used most often with dosages ranging from 10 to 40 mg/L. Polymers constitute another group of coagulants. The polymers attach to different particles, bringing them together. Compound volumes of 1 to 5 mg/L are usually sufficient to increase the settling rate by two- or threefold. Another advantage of using the polymers is that the solids capture is improved.

While coagulants improve flocculation, the main problem to overcome is the effect of low concentration on the frequency of particle contact. The equipment design must solve this problem. The type of clarifier used in the groundwater treatment system will depend on the concentration of solids.

Settling Equipment

There are several types of settler designs that can be employed to remove suspended solids. This book reviews the following four designs to identify the major components of each:

- Clarifier/thickener
- Flocculating clarifier
- Solids contact clarifier
- Lamella

On short-term groundwater treatment projects, the design engineer may not want to spend the money on a preconstructed settling tank. An existing tank or a portable tank can serve as a quiescent tank in which solids can settle. For successful settling, the velocity of the water must be reduced to a point at which solids will settle by gravity. A rough guide regarding surface loading rates is that they should range from 0.2 to 0.7 gpm per square foot of surface area for particle removal.

A clarifier/thickener is the simplest of the four settler designs. A clarifier/thickener must perform several tasks. First, the water with the suspended solids must enter the tank without causing turbulence in the tank and reagitating already settled solids. Next, the water must be

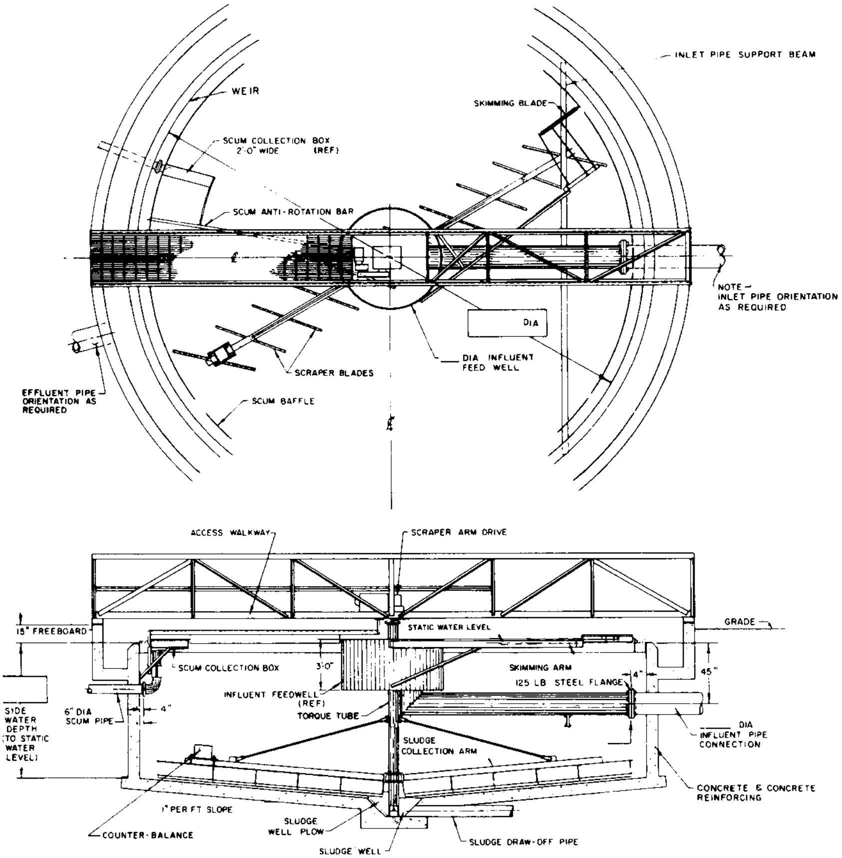

FIGURE 5-7. Center feed clarifier. (Courtesy of Smith & Loveless, Inc.)

evenly distributed throughout the tank to make maximum use of the surface area of the clarifier. The supernatant must then be collected and removed from the tank. Finally, the solids must be thickened and removed from the tank.

Figure 5-7 depicts a standard “center feed” clarifier. The water enters into the center feed well. The feed well protects the contents of the clarifier from the energy contained in the incoming water. If the flow is to be introduced into the side of the tank, a plate or half-sphere (outside facing out) should be placed at the inlet pipe. This will serve the same energy dissipation function as the feed well.

The key to water distribution in the clarifier includes both the influent section and the effluent collection section. The influent must be introduced as specified above. The effluent must be collected over as large a surface area as possible in the tank. This is accomplished using a saw-toothed weir atop a trough. The maximum overflow rate should be limited to 13 gpm per feet of weir length. Lower levels are always better. The weir should be level throughout the tank to ensure proper distribution of the water in the tank. A flat weir can be used, but it is more difficult to adjust to the correct height throughout the clarifier. The troughs are connected to a single pipe that exits from the clarifier.

The solids settle to the bottom of the tank. With flocculating solids, it is important to have sufficient depth for the floc to grow inside the clarifier. The depth also allows the solids to concentrate before they are removed from the tank. The less liquid intermixed with the solids, the less material that will need to be sent for disposal. The solids must be moved to one location for removal from the tank. The clarifier depicted in Figure 5-7 uses scrapers on the bottom of the tank to push the solids toward the center of the tank. The solids are collected in a sludge well and exit the tank through a pipe. An alternative for scrapers is to slope the bottom of the tank at 60 degrees to a central point. This is called a hopper bottom clarifier and is viable only for small designs.

Clarifiers should be designed at 0.2 to 0.7 gpm per square foot of surface area. The maximum diameter of a portable clarifier is 12 feet (the wide load on a truck). Therefore, the maximum flow rate of a portable clarifier is about 80 gpm. Multiple units or a site-erected clarifier will have to be employed for flows above this level.

Flocculating Clarifier

A flocculating clarifier has all the same components as a regular clarifier. The only difference is that the influent well is larger. Gentle mixing is performed in the influent well as this well is the flocculation zone inside the clarifier. A standard clarifier is good for solids of 1,000 mg/L and above. Below that level, the clarifier loses efficiency. The flocculation section extends the efficient operation down to 500 mg/L. The specific concentration for both operations depends on the settling rate of the solids. The flocculation section can be positioned outside the clarifier. Important design considerations include a process for the gentle mixing and transfer of water to the clarifier without any shear forces on the floc that has been formed.

Solids Contact Clarifier

The solids contact clarifier combines already settled solids with incoming solids. The key to settling is large particles. The settled solids, of which a portion is recirculated, act as the core onto which the new solids attach. There are also more contacts between solids than would

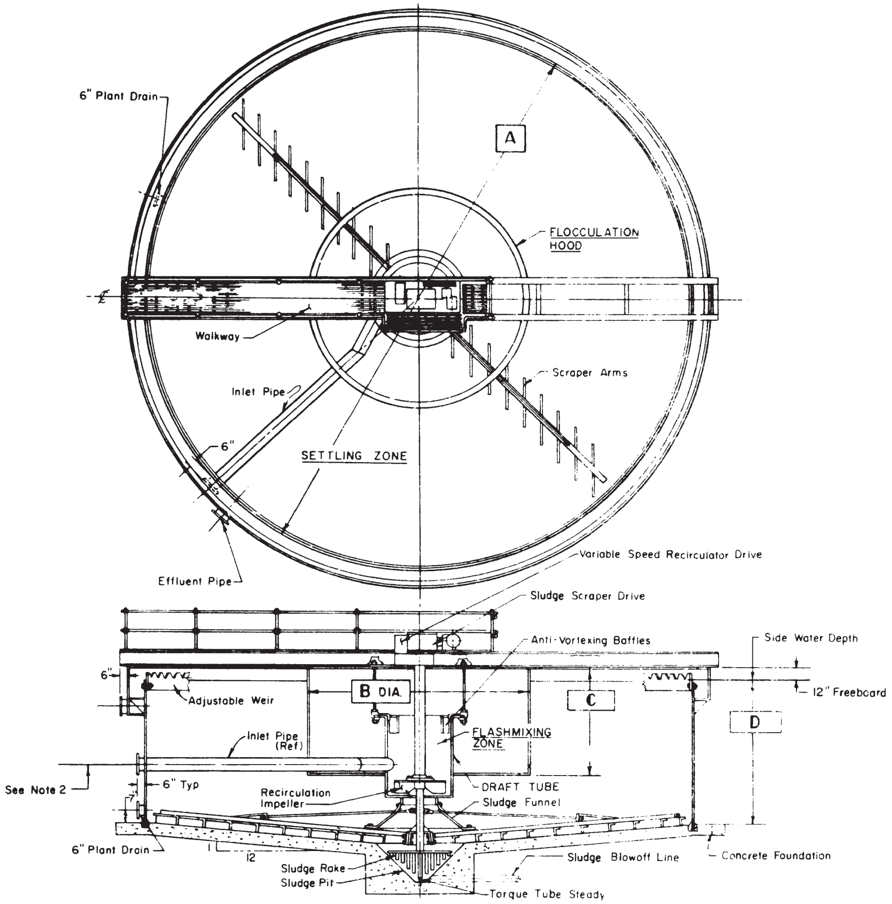

FIGURE 5-8. Solids contact clarifier. (Courtesy of Smith & Loveless, Inc.)

be provided with only a low-concentration influent alone. Figure 5-8 shows a solids contact clarifier. Two advantages are realized with this design. First, lower suspended solids can be introduced to the clarifier and removed efficiently. Second, the recycle of the solids makes more efficient use of the chemicals added to the water. A 20- to 30-percent savings can be realized. The solids contact clarifier can be designed at up to 1.0 gpm per square foot and influent solids as low as 100 mg/L.

Lamella Clarifier

The lamella clarifier has the highest flow rate per tank surface area of all the clarifier designs. The lamella design is based on all of the basics of clarification except one. It emphasizes the fact that when the

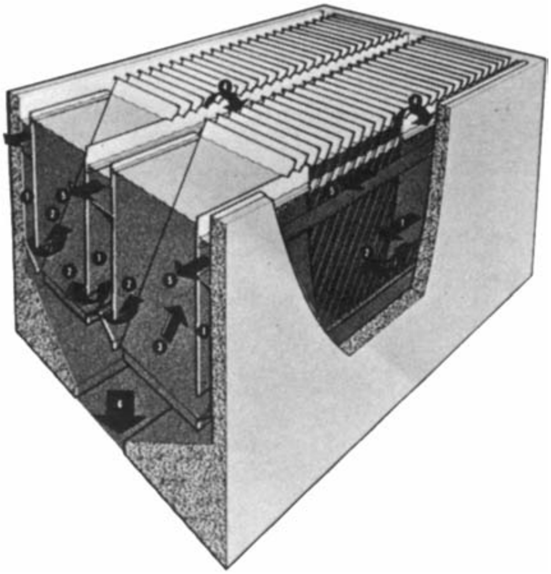

FIGURE 5-9. Lamella clarifier. (Courtesy of Graver Water.)

solids hit the bottom of the tank, they are removed from the water. Instead of putting the bottom 10 feet from the top, the lamella puts the bottom 2 to 4 inches from the top.

Figure 5-9 illustrates a lamella clarifier. The water enters the sides of the plates and is equally distributed to all plates. The water travels up the plates, and the solids settle onto the plates. When the solids have settled on the plates, they are removed from the water. The solids on the plate continue down the plate as in a hopper bottom clarifier. The slope of the plates is from 45 to 60 degrees.

What makes the lamella design so powerful is that the theoretical settling area is the projected area of the plates, Figure 5-10, and the projected area of all the plates is additive. The resulting projected area can be ten times the liquid surface area of the tank; therefore, up to ten times the liquid flow can be applied to the same size tank.

The solids that have been removed by the plates fall off and enter the thickening section. The thickener can be a hopper bottom design or have scrapers. The removal efficiency is the same as a standard clarifier. The design engineer uses the same laboratory data to design the lamella but uses the projected area of the plates for the surface-loading rate.

For flows that are small enough for a portable clarifier (80 gpm), the lamella is probably not economical. When the tank is small, the cost

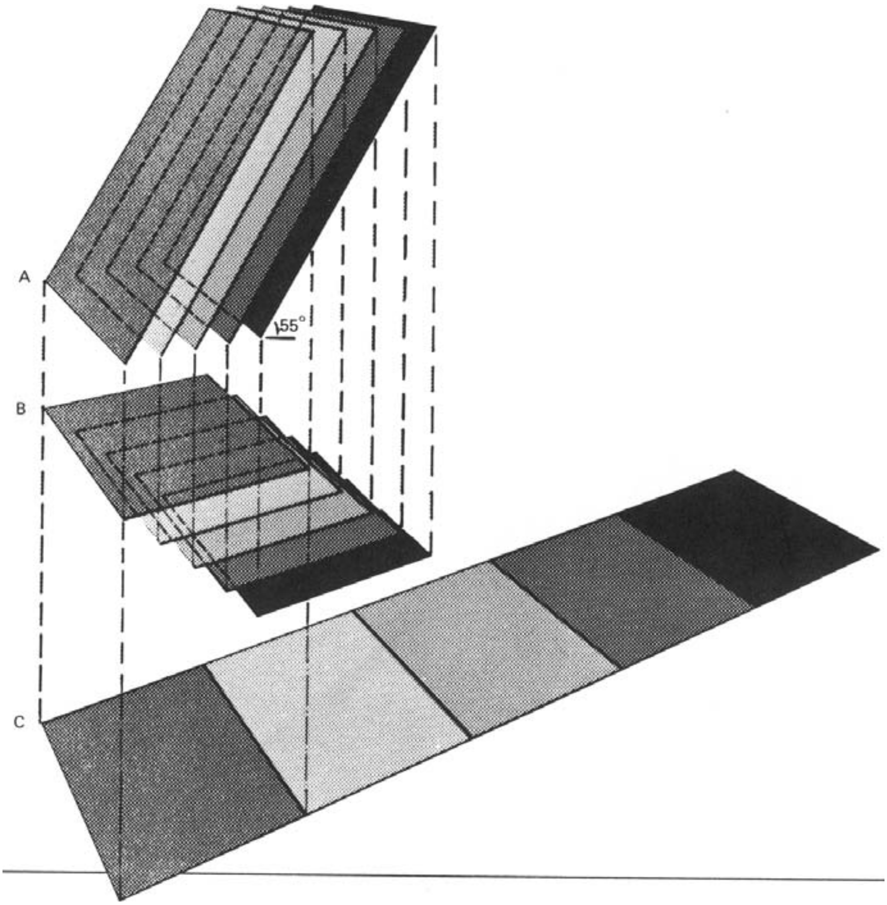

FIGURE 5-10. Theoretical settling area of a lamella clarifier. (Courtesy of Graver Water.)

of the plates makes the unit relatively expensive. However, for larger flows, the resulting savings in total size of the tank makes the cost of the plates economical. Even in large sizes, the lamella is a portable clarifier. The unit increases in length as more plates are added to increase the projected surface area, and the 12-foot wide-load limit can be maintained for large units.

Filtration

All suspended solids are not typically removed by settling. Even the most efficient clarifier will leave 5 to 10 mg/L of suspended solids in the water. This concentration is generally acceptable for reinjection or discharge to a receiving water body or a POTW. However, when the water is to be used for drinking water or process water, even this low concentration is too high. The suspended solids must be removed by other technology (i.e., filtration). Filtration is also typically required as pretreatment for the implementation of such technologies as carbon adsorption reverse osmosis and other technologies requiring water with minimal amounts of suspended solids.

Low suspended solids must be filtered from the water. The simplest form of filtration is to pass the groundwater through a bed of sand. The suspended solids attach to the sand particles, and the water continues through the bed. It is important for the design engineer to realize that a sand filter does not just strain the solids from the water. A sand filter removes suspended solids by several mechanisms, including straining, adsorption, flocculation, and sedimentation.

The straining process occurs in the top few inches of a bed near the water/filter media interface. Only the large particles are removed in this manner because they are too big to penetrate the voids between the media. Some of the smaller particles will be removed deeper in the bed as particles agglomerate in the voids. However, it should be noted that straining is not the principal removal mechanism of a filter.

Adsorption (solid–solid contact) is the principal removal mechanism in filtration operations. The adsorption mechanism is similar to the way colloidal particles combine to form a floc. Adsorption is dependent on the physical characteristics of the suspended solids and the filter media, such as filter grain size, floc size, adhesive characteristics, and the intensity of surface change on both the suspended solids and filter media.

Flocculation and sedimentation within the voids of the media also occur but are of limited importance. With the tremendous amount of sand in the path of the water, the chances of contact are greatly increased. So, even with very low concentrations of suspended solids, the particles will come into contact with a sand particle and be removed.

A polymer addition upstream of the filter may increase the removal efficiency of the filter. Polymers as filter aids can be either coagulants or flocculants. Coagulants are more commonly used. Coagulants are adsorbed onto the filter media surface and enhance the adsorption process. Typical coagulant feed rates when used as filter aids are from 0.25 to 1 ppm. Flocculants as filter aids strengthen the floc formed in the filter, improving shear stability. They are fed at dosages from 10 to 100 ppb. Overdosage can cause filter blinding. The removal efficiency of the filter can be improved from 50 to 90 percent by using these techniques.

As the filter bed becomes clogged and the pressure differential across the bed increases, the filter bed must be backwashed. Clean water is pumped at a fast rate through the sand bed in the direction opposite the flow of the wastewater. The sand bed is fluidized, and the turbulence in the bed breaks off the particles attached to the sand. The water flushes the suspended solids from the filter. The sand is heavier and larger than the suspended solids and remains in the tank. When an increase in shear forces is required to remove the suspended solids, air is added to the sand bed with an air scour system to increase turbulence. An air scour system should be included in most filters to enhance the backwashing capabilities used in groundwater treatment systems. The slight increase in capital expense for an air scour system is invaluable because of the potential problems it helps to eliminate.

A good example of sand filter operation occurred at a federal Superfund site. A pilot plant was designed for 100 gpm and included an air stripper, followed by a sand filter and a carbon adsorption unit. The sand filter was a modified pressure vessel without an air scour system for backwashing.

The treatment system was designed to treat several VOCs. The air stripper and the carbon adsorption units were chosen for organic removal. The sand filter was designed to protect the carbon adsorption bed from becoming fouled with suspended solids. The groundwater contained 4 to 7 mg/L iron in addition to the organic contaminants that the system was designed to remove.

The sand filter failed to protect the carbon bed under field operation. Two main problems caused this failure. First, the iron had not completely oxidized to the insoluble form before it reached the sand filter. The iron oxides precipitated out in the carbon adsorption bed. Second, the sand filter backwashing operation could not remove all of the iron solids from the sand bed.

The air stripper served as the main source of oxygen for the groundwater. This led to some iron oxide precipitation on the media in the air stripper (see Chapter 2, Air Stripping section for a full review of this problem), and the large production of iron suspended solids from the air stripper. However, the air stripper provided only 4 to 7 minutes of reaction time for the iron to oxidize before it reached the sand filter. As discussed earlier in this chapter, this is less than the recommended 30 minutes reaction time for full oxidation. Therefore, some of the iron continued in the soluble form through the treatment system. But because there was oxygen present in the water, the oxidation reaction continued. Therefore, some of the iron bypassed the sand filter in the soluble form and then precipitated in the carbon adsorption unit.

The second problem came from backwashing the sand filter. Iron can be very difficult to remove from sand particles. This is especially true if some of the solid iron actually formed on the sand itself. The original design for the sand filter included only a water backwash for the removal of the suspended solids. The water backwash operation was not able to provide the shear forces needed to dislodge the iron solids from the sand. The solids built up in the sand bed. Backwashing was required more and more often. Finally, "rat holes" occurred in the sand bed, the water short circuited through the bed, and the groundwater was not treated.

Both of these problems caused the carbon bed to fail as a result of suspended solids fouling. The pilot plant was modified to include air scouring in the sand filter, and the pilot test was completed. For the full-scale design, preaeration with a retention time of thirty to forty minutes was implemented to completely oxidize the iron. The suspended solids were then removed in a continuous backwashing sand filter, protecting the air stripper and carbon units.

As shown in Figure 5-11, a dual-media filter consists of 1 foot of anthracite and 1 foot of sand. In a sand filter, there would be 2 feet of sand instead of 1 foot of sand and 1 foot of anthracite. The water enters the top and hits a splash plate. The splash plate guarantees that the water falling onto the sand does not disturb the bed of sand. Sand filters can also be run in the upflow mode. Upflow continuous backwashing sand filters are described later in this section. There are advantages and disadvantages to this flow pattern, but most sand filters today are the downflow variety. The distance from the top of the filter chamber to the top of the sand should provide enough room for a 50-percent expansion of the sand bed during backwashing.

When a filter bed is backwashed, the smallest particles end up on top of the bed. As solids are filtered out of the water, they build up in the sand. The smaller the sand particles, the faster the solids build up. The solids will finally fill most of the void spaces in the sand bed. When this happens, the primary filtration mechanism switches from adsorption to straining. Straining of solids from the water takes a great deal of force; the water builds up on top of the bed; and the differential pressure increases. Gravity filters are normally set up with a water column above the bed to force the water through the sand. These columns can be a maximum of 15 feet above the sand but are typically 7 to 10 feet, with the minimum being 3 feet.

There are two main ways to extend the use of the sand bed. The first of these is to place a bed of coal above the sand bed, Figure 5-11. This is referred to as a dual-media filter. The coal particles are slightly

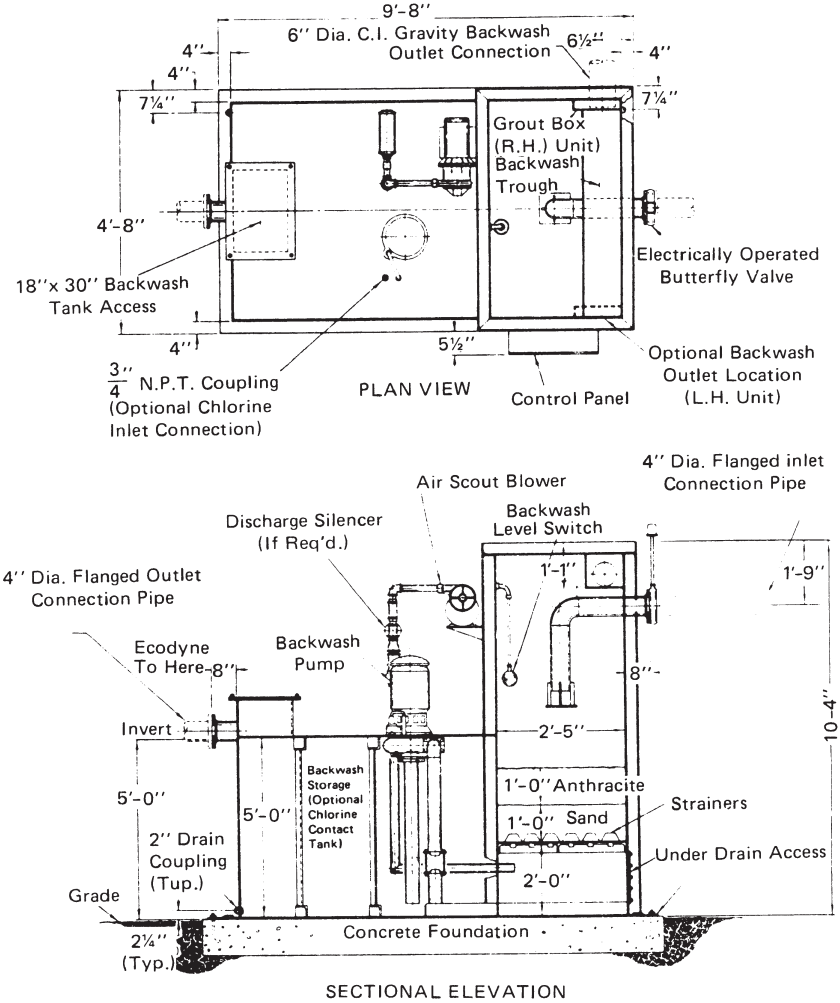

FIGURE 5-11. Dual-media gravity filter. (Courtesy of Smith & Loveless, Inc.)

larger and lighter than the sand. When the beds are backwashed, the larger coal particles end up on top of the sand. Suspended solids are removed by the coal before they get to the sand, thus extending the length of time between backwashing. When a filter is planned for use after a biological system or with a high concentration of suspended solids (50 to 100 mg/L), a dual-media filter is recommended.

The second way to extend the time between backwashes is to seal the filter tank and use a pump to increase the pressure available for forcing the water through the filter bed. Pressure filters are good for high-concentration suspended solids, 100 to 250 mg/L. The filter run must be long enough to produce sufficient water for backwash. The lower the percentage of processed water used for backwash, the better. A maximum of 10 percent of the processed water should be used for backwash, and the design should strive for 2 to 5 percent. On the other hand, the filter should be backwashed every 24 to 48 hours. This will ensure that the bed remains clean and that there is no buildup of solids in the filter bed. The choice between sand, dual media, and pressure should be made to address these system limitations.

Continuing down the filter, the next section is the sand support and backwash water distribution. There are two main ways to accomplish these functions. Figure 5-11 depicts the method that uses strainers atop a support plate. The sand cannot get through the slots in the strainer. The backwash water and air are equally distributed to all of the strainers. The second method is to place distribution pipes in a gravel bed under the sand. Once again, there are advantages and disadvantages to both designs. For the portable groundwater market, the system with the strainers is probably the better system.

The final section of the filter is the backwash storage section. The water to be used for backwashing should be relatively clean of suspended solids. The water that has already been processed by the filter can be used for backwash. Backwash water should flow at 15 gpm per square foot of filter surface area for 5 minutes. This water can be stored beside the tank and pumped at the necessary rate, or the water can be stored above the filter and allowed to flow back through the filter by gravity. Air, if desired, should flow at 3 to 8 cfm per square feet of surface area for 5 minutes. A blower should be used for supplying the air.

One final advantage of the sand and dual-media filters is that their operation can be set up to be automatic. A pressure or time setting can be used to initiate the backwash cycle. No operator attention is necessary for the proper operation of these filters.

An alternative to the standard gravity and pressure filters is a continuous backwashing sand filter. Two types of these filters are currently available: a downflow and an upflow model. Both work on the same general principal: the filter media (sand) is continuously cleaned by recycling the sand through an airlift sand washer. An upflow model is presented in Figure 5-12. These types of filters eliminate the need for backwash pumps, backwash storage, and valves associated with the backwash operation.

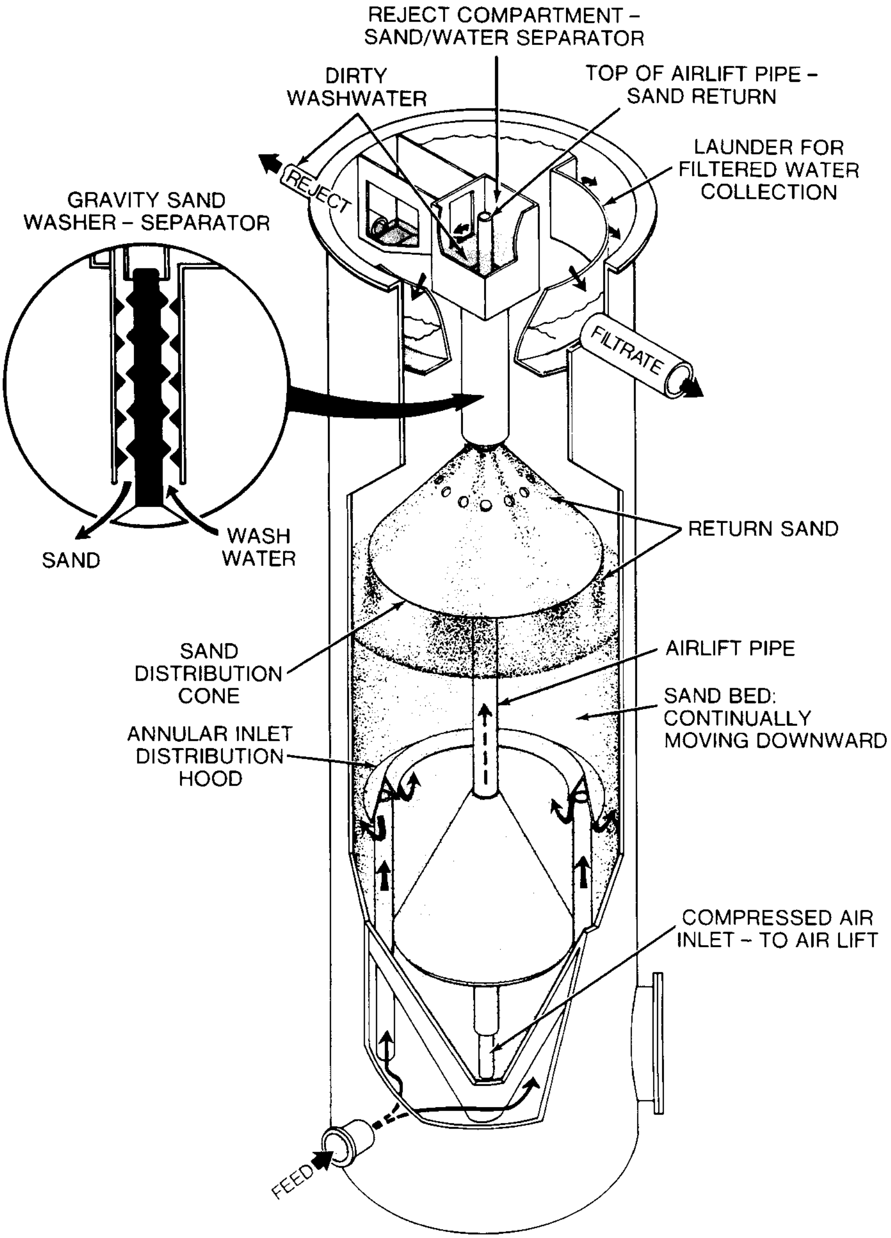

FIGURE 5-12. Upflow continuous sand filter. (Courtsey of Parkson Corp.)

Filtration by Straining

Other types of filter technology are available for groundwater treatment. Sand filters are based on adsorption and avoid straining as a mechanism of suspended solids removal. However, several filter designs are based on straining. Bag filters, cartridge filters, and cloth filters all strain the suspended solids from the water.

Bag filters are basically a filter cloth in the shape of a bag. The bag is placed in a pressure vessel with a wire support for the bag. The water enters the center of the bag, and the filter cloth strains the suspended solids from the water. The solids build up in the bag. When the pressure drop is too high, the bag is removed and cleaned or replaced.

Bag filters have low filter surface-to-volume ratios but a large solids storage area. This type of design is applicable to relatively large discrete solids. When the solids are small or if they are gelatinous (i.e., bacteria), the filter cloth will clog quickly. Large particles (i.e., sand) typically build up in the bag without large pressure drops.

Cartridge filters use the same straining mechanism but have a larger filtering surface area. The groundwater flows from the outside in through the cartridge. The filter can be composed of several types of material and can be designed for surface straining or depth removal. The best design for groundwater application is usually the wound type of depth cartridge. This design has a greater loading capacity and will remove small particles. Once again, if the pressure drop is too high, the cartridges should be cleaned or replaced. Surface cartridges can be cleaned, but depth filters usually have to be replaced.

Both bag and cartridge filters are generally used to protect the next unit of operation in the treatment system from solids fouling. Groundwater treatment does not normally require the low suspended solids concentration that these filters can achieve. The main reason that these units are used for groundwater systems is their low capital costs. Because groundwater flows are normally small, bag and cartridge filters can be a very economical way of removing suspended solids. Small sand filters (10 gpm) with automatic air/water backwash will cost about $10, 000. Bag or cartridge filters will cost about $1,000 for the same flow range. Bag and cartridge filters will have the added operating costs for cleaning or replacing the filter. The design engineer will have to perform a cost analysis to see which system is applicable to a particular situation.

The cloth filter can also be used to remove suspended solids. In this case, a filter cloth is placed across the groundwater flow, removing the suspended solids. These units are limited to low pressure drops across the filtering area and are, therefore, limited in solids capacity. The main example of this technology use for groundwater treatment is in conjunction with the diffused aeration systems discussed in the Air Stripping section of Chapter 2.

MEMBRANE PROCESSES

Membrane processes use thin barriers or interfaces for separating chemical species from water. The straining filters described in the previous section are in essence membranes; however, they are considered filters because of the size of the particles they are capable of separating from the water and because they rely on mechanisms such as adherence of the particles to the filter media or accumulation of a fouling layer to remove the particles.[7] The term *filter* is typically used when the particle sizes being removed from the water stream are greater than 1 micrometer (μm) to 10 μm.[8] Membrane processes are used when smaller particles, chemical molecules, or biological organisms must be separated from water.

Specified operating parameters consist of the following:

- Pressure or vacuum, which is generally dictated by membrane material
- Recovery rate, which is the percentage of feed water converted to product water
- Flux rate, which is the flow rate of the water that passes through a unit area of the membrane

The flux rate of water through a membrane is proportional to the pressure differential across the membrane. The higher the pressure, the higher the flux rate for a given membrane. The flux rate also depends on the material thickness of the membrane and the temperature of the feed water. Flux rates should be specified conservatively to provide for the long-term operation of the membrane.[9]

Several types of membranes exist, and these can be grouped into the following categories[7–9]:

- *Isotropic membranes* are membranes that consist of a single material throughout their thickness.
  - *Microporous membranes* are rigid structures with a high degree of voids, randomly interconnected, with sizes ranging from 0.01 to 10 μm. The primary separation function is by size, and these membranes are often used in microfiltration or ultrafiltration. Ceramic

  membranes are a special class of microporous membranes that are used when chemical stability and thermal stability are required.
  - *Nonporous, dense membranes* are films through which solutes permeate by diffusion using driving forces of pressure, concentration, or electrical potential. The primary separation mechanism is the solutes diffusivity and solubility in the membrane material. Many reverse osmosis membranes are dense membranes.
  - *Electrically charged membranes* may be either microporous or dense membranes whose pores carry positively or negatively charged ions. The primary separation mechanism for electrically charged membranes is by the rejection of like-charged molecules or ions. Electrodialysis uses electrically charged membranes.
- *Anisotropic or asymmetric membranes* are membranes that consist of a thin membrane layer mounted on a porous, thicker substructure that has a much higher flux rate than the surface membrane. The substructure acts solely as a support to the surface membrane that controls the separation properties of the membrane.

There are four types of membrane processes that are well established and potentially applicable to the treatment of groundwater or industrial process waters.

- Microfiltration
- Ultrafiltration
- Reverse osmosis
- Electrodialysis

The first three membrane processes are differentiated by the size of the pore diameter of the membrane (Figure 5-13). Electrodialysis membranes are different from the previous three processes in that they use electrically charged membranes for separation.

Microfiltration

Microfiltration is used to remove particles that range in size from 0.1 to 10 μm. These membranes typically have a pore size ranging between 0.1 and 0.2 μm.[7] The first microfiltration membranes were constructed of cellulose acetate and nitrocellulose.[8] These materials are still used today; however, additional materials of construction include polyvinylidene fluoride, polyamides, polyolefins, and polytetrafluoroethylene, as well as inorganic materials such as alumina, glass, and carbon-coated zirconia.[7,8,10]

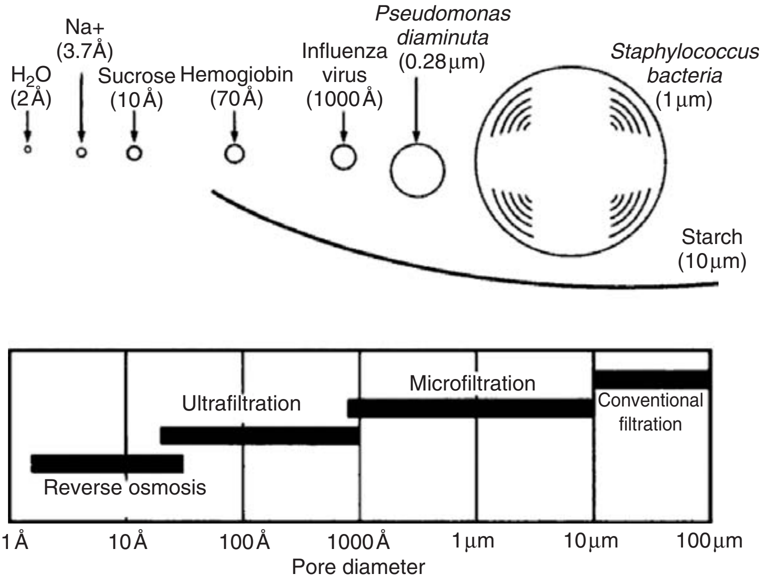

FIGURE 5-13. Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic. (*Source*: Baker, *Membrane Technology and Applications*, 2nd edition, Wiley, 2004.)

Two types of microfiltration processes are commonly used: inline filtration and cross-flow filtration. Inline filtration is most often used when solutions contain less than 0.1 percent solids greater than 1 to 10 µm.[8] In this process, the entire solution is forced through the inline membrane, and the rejected particles collect on the surface and through the depth of the filter medium. As particles are rejected and build up on the membrane, more pressure is required to force the solution through the membrane. When excessive pressure buildup occurs, the membrane is taken offline and cleaned or disposed. Single-use membranes are routinely used for microfiltration because they are inexpensive compared to ultrafiltration or reverse osmosis membranes. Costs for single-use microfiltration membranes typically range from $3 to $4 per square foot of membrane.[8]

Cross-flow filtration is used when solutions contain greater than 0.5 percent solids[8] and is more often applied in ultrafiltration and reverse osmosis applications. In cross-flow filtration, only a portion of the solution is forced through the membrane, while the remainder is flushed across the surface and used to sweep away the rejected particles. The solution that passes through the membrane is called the permeate, while that portion that is rejected is called the retentate or brine. In this type of process, the rejected particles become concentrated in the retentate, and this waste stream must be managed as a by-product of the filtration process.

During the 1960s and 1970s, inline plate-and-frame modules were used to apply microfiltration processes. In these systems, the membrane is held between two plates and sealed with gaskets. These systems provide limited surface area for filtration and are labor intensive to maintain because they require disassembly and reassembly to replace the membrane after each use. These types of systems are still used in laboratory settings where only small volumes of solution are processed.

Today, the typical microfiltration application uses disposable cartridges consisting of a pleated membrane wrapped around a supporting core. The cartridges provide a much larger surface area for filtration than plate-and-frame modules. A typical wrapped cartridge is 10 inches long and 2 to 2.5 inches in diameter and provides about 3 square feet of surface area for filtration.[8] For large applications, multiple cartridges can be connected in parallel to process higher flow rates. Additionally, to extend the life of these disposable filters, multiple cartridges with progressively smaller pore sizes may be used in series. In this type of application, the first cartridge contains a coarse filter and removes the largest particles, while subsequent polishing cartridges capture smaller particles.

Microfiltration systems are typically operated as constant-flux systems. Feed pressures are generally fixed at a high level (e.g., 120 psi), and the permeate pressure is initially set at a slightly lower level (118 psi). As the permeability of the membrane decreases because of particle capture, the permeate pressure is lowered, thus increasing the driving gradient across the membrane to maintain a constant flux of permeate.

Ultrafiltration

Ultrafiltration is used to remove macromolecules and colloid-sized particles from solutions. Pore sizes of the ultrafiltration membranes used most often range in size from 0.01 to 0.05 μm, but smaller pore sizes are possible.[7] The lower end of the pore size range for ultrafiltration membranes has been reported as 10 to 50 angstroms (Å) (0.001 to 0.005 μm).[7,8]

Another way to characterize the performance of ultrafiltration and reverse osmosis membranes is by the molecular weight cutoff and is measured in daltons.[7] A membrane rated for 10,000 daltons will theoretically removal all compounds with a molecular weight greater than this value. The molecular weight cutoff ratings for ultrafiltration membranes can range from 1,000 to 500,000 daltons, but most ultrafiltration membranes used for water treatment have a molecular weight cutoff of 100,000 daltons.[7]

The first ultrafiltration membranes were constructed of nitrocellulose; additional materials of construction now include cellulose acetate, polyacrylonitrile copolymers, aromatic polyamides, polysulfone, polyvinylidene fluoride, polytetrafluoroethylene, and nylon.[7,8,10] Ceramic-based ultrafiltration membranes that are resistant to high temperatures and can be cleaned with harsh chemicals to control fouling have recently been developed.[8]

The cost of ultrafiltration membranes ranges from \$20 to \$50 per square foot of membrane for tubular plate-and-frame modules constructed of polymeric materials. The newer, ceramic-based membranes are more costly, ranging from \$100 to \$200 per square foot of membrane. Because the cost of ultrafiltration membranes is 10 to 100 times higher than microfiltration membranes, they are not used in a disposable manner. The typical service life of an ultrafiltration membrane is 2 to 3 years. To achieve this service life, several techniques to control membrane fouling must be considered in the design and operation of the systems.

One method used to control membrane fouling is to design and operate the membranes using a cross-flow filtration process. As described earlier, only a portion of the solution is forced through the membrane in cross-flow filtration, while the remainder is flushed across the surface and is used to sweep away the rejected particles. Even when using cross-flow filtration (because ultrafiltration membranes are used to separate macromolecules and colloidal material from solutions) fouling will occur.

One of the primary membrane fouling mechanisms is the deposition of retained material on the membrane surface caused by a phenomenon called concentration polarization. Within seconds of initiating operation, a gel layer forms on the surface of the membrane. This gel layer acts as a secondary barrier to flow, and the flux rate through the membrane immediately drops on average to 10 percent of the pure water flux rate.[8] With continued operation, further reductions in flux may be observed as a result of the consolidation of the gel layer.

Additional membrane fouling control techniques include regular membrane cleaning, backflushing, and using membranes that resist adhesion.[8] Membrane cleaning cycles vary based on the solution being processed but can be as frequently as daily in food industry applications. One of the simplest cleaning methods is to circulate a cleaning solution through the membrane modules for one to two hours. Alkaline cleaning solutions followed by hot detergent solutions are often used to clean membranes fouled by organic polymer colloids or gelatinous materials. Conversely, insoluble metal hydroxide fouling is treated using citric or hydrochloric acid solutions. Following the cleaning procedure, the membrane systems are typically flushed thoroughly with water to remove traces of the cleaning solution and detergents.

Backflushing is a cleaning technique that can be used on ultrafiltration membranes that will not be damaged by reversing the flow through the membrane. Capillary and ceramic membrane modules can be backflushed, but spiral-wound modules are too easily damaged and should not be backflushed.[8] Backflushing membranes involves slightly overpressurizing the permeate side of the membrane (5 to 15 psi) and forcing water from the permeate side to the feed solution side.

Reverse Osmosis

Reverse osmosis separates a solute from a solution using a pressure gradient to force the solvent through the membrane. Reverse osmosis membranes have the smallest pore sizes of the membrane types discussed here. Pore sizes typically range from 5 to 15 Å (0.5 to 1.5 μm)[10] and have nominal molecular weight cutoff ratings of less than 100 daltons.[7]

The selection of a membrane material, the configuration, and the operating conditions are critical to obtaining the desired results. The most common reverse osmosis membrane materials are cellulose acetate, polyamide, and thin film composite.[7,10] Cellulose acetate membranes are susceptible to biodegradation and must generally be used over a narrow pH range of 4 to 8.[7] Biodegradation and biofouling can be controlled using low doses of chlorine (0.5 mg/L or less) without damaging the membrane. In contrast, polyamide membranes are not subject to biodegradation and operate over a wider pH range; however, these membranes are susceptible to attack by strong oxidants.[7]

The various configurations for membranes consist of spiral-wound, hollow fiber, tubular, and plate and frame (Figure 5-14). As the name suggests, hollow-fiber modules comprise several hundred to several thousand long, thin strands of membrane material bundled together. These modules may be operated in either an "outside-in" or "inside-out" configuration and are more frequently used for microfiltration and ultrafiltration membranes.[7] The spiral-wound configuration is most frequently

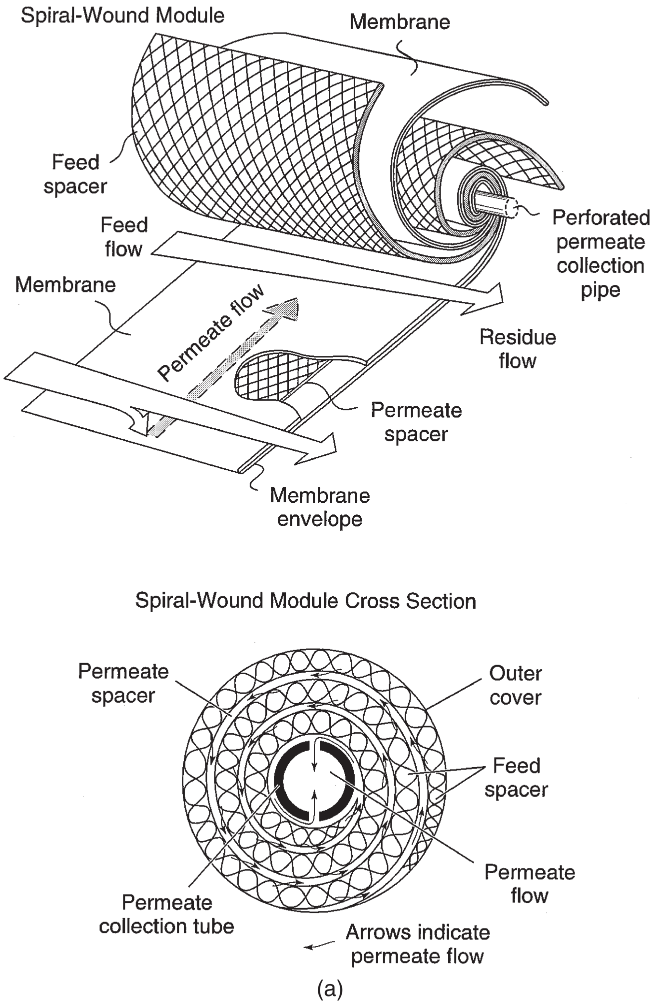

FIGURE 5-14(a). Exploded view and cross-section drawings of a spiral-wound module. Feed solution passes across the membrane surface. A portion passes through the membrane and enters the membrane envelope where it spirals inward to the central perforated collection pipe. One solution enters the module (the feed) and two solutions leave (the residue and the permeate). Spiral-wound modules are the most common module design for reverse osmosis and ultrafiltration as well as for high-pressure gas separation applications in the natural gas industry. (*Source*: Baker, "Membrane Technology and Applications, 2nd Edition", John Wiley & Sons, 2004.)

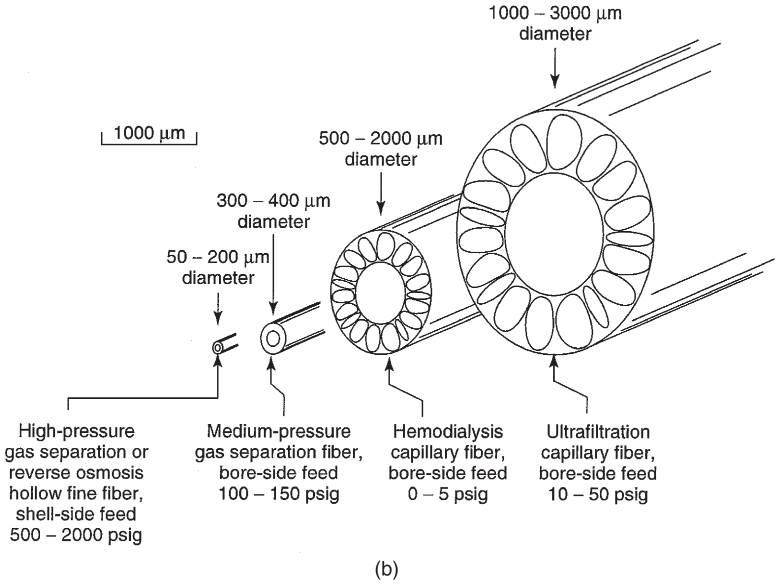

FIGURE 5-14(b). Schematic of the principal types of hollow fiber membranes. (*Source*: Baker, "Membrane Technology and Applications, 2nd Edition", John Wiley & Sons, 2004.)

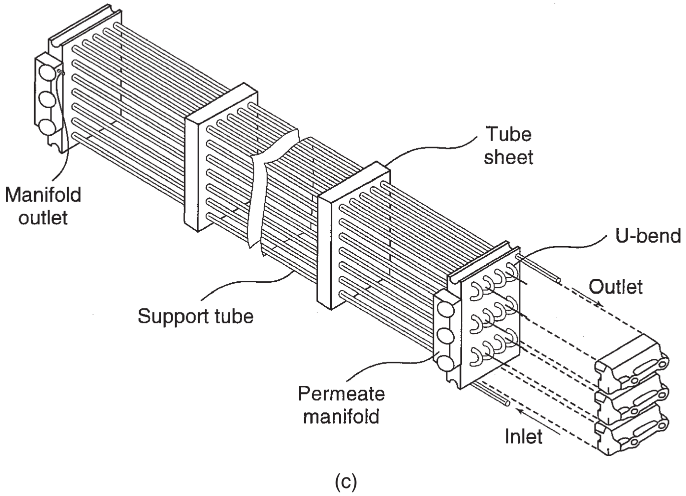

FIGURE 5-14(c). Exploded view of a tubular ultrafiltration system in which 30 tubes are connected in series. Permeate from each tube is collected in the permeate manifold. (*Source*: Baker, "Membrane Technology and Applications, 2nd Edition", John Wiley & Sons, 2004.)

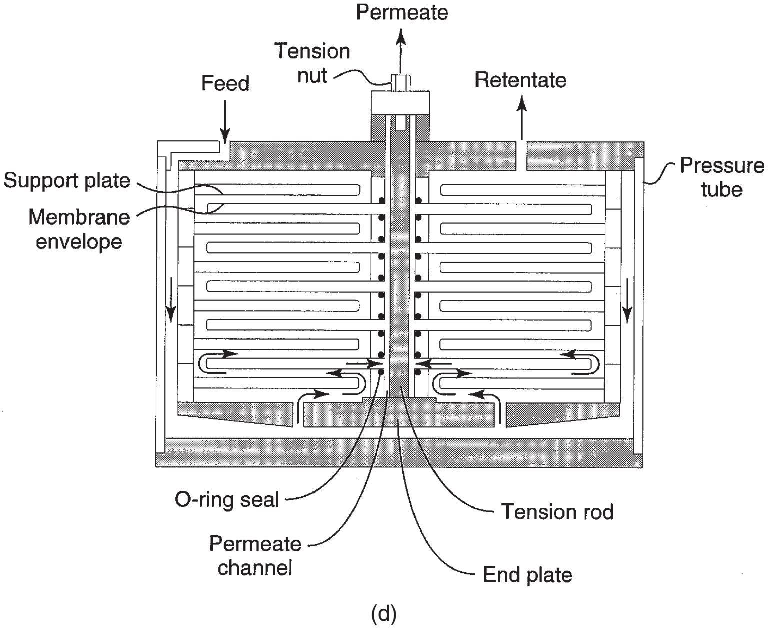

FIGURE 5-14(d). Schematic of a plate-and-frame module. Plate-and-frame modules provide good flow control on both the permeate and feed side of the membrane, but the large number of spacer plates and seals lead to high module costs. The feed solution is directed across each plate in series. Permeate eneters the membrane envelope and is collected through the central permeate collection channel [111]. (*Source*: Baker, "Membrane Technology and Applications, 2nd Edition", John Wiley & Sons, 2004.)

used for reverse osmosis applications. Spiral-wound modules consist of sheets of membrane layered between spacer sheets for carrying permeate and feed/reject water streams.

These layers of alternating sheets are wrapped around a perforated carrier pipe that ultimately acts as the receiver for the permeate. The entire spiral-wound module is encased in a pressure vessel.

Reverse osmosis can be utilized to remove most inorganic contaminants from groundwater and is often used for the desalination of salt water for drinking.[7] Wastewater must undergo extensive pretreatment prior to reverse osmosis; therefore, reverse osmosis is expensive to operate and is typically not utilized for general metals treatment. Reverse osmosis is used to recover metals in plating operations, but its use should be limited to nitrates, sulfates, total dissolved solids, and naturally occurring inorganics in groundwater.

Reverse osmosis is also not a preferred method for treating small concentrations in organic compounds. Low molecular weight organic compounds pass through the membrane at rates far greater than inorganic compounds. Currently, research is being conducted to enhance the effectiveness of organic compound treatment with reverse osmosis. Limited successes have been achieved with the high molecular weight organic compounds.

Reverse osmosis systems are readily available. They are expensive to run because of the high pressures required, typically from 200 to 400 pounds per square inch gauge (psig) and the stringent pretreatment requirements. The pH generally must be maintained between 5.5 and 7.5 to minimize fouling. Suspended solids have to be removed to the maximum extent possible. Great care must also be taken to ensure that no precipitation occurs in the reverse osmosis module.

Reverse osmosis was tested on groundwater at a site regulated under the Resource Conservation and Recovery Act (RCRA) to remove sulfates and nitrates from an aquifer contaminated with VOCs.[9] Effluent requirements became the controlling factor in the selection of the design. Nitrate concentrations had to meet drinking water standards of 10 mg/L, while sulfate concentrations only had to reach 250 mg/L Even with a total solids concentration between 10,000 and 20,000 mg/L in the influent, the effluent nitrate requirements controlled the system setup.

One of the problems with the operation of the system was that nitrate removal was supposed to be maximized by increasing the pH. However, at raised pH levels, precipitation occurred in the system and fouled the membranes. A pH of 6.5 was finally used as a compromise. Under these conditions, a two-stage system was required to meet the nitrate requirements.

Electrodialysis

Electrodialysis is a combination of membrane technology and ion exchange technology. Electrodialysis uses ion exchangers in membrane form. The driving force across the membrane is provided by electric current. The ions are removed from the water, and they pass through the membrane, attracted by the opposite electric charge on the other side of the membrane.

The advantages of the system are that the residence time controls the amount of dissolved solids removed and that the system can be run continuously with no regeneration required. The disadvantage of the system is that the water must carry an electric current. The cleaner the water is, the more resistant it is to the current, which increases the cost of operation.

Additional Considerations for Membrane Process Design

Three main areas are often overlooked when considering membrane processes: (1) pretreatment of the feed stream to remove excessive amounts of suspended solids or other membrane fouling compounds; (2) post-treatment conditioning of the permeate, which is often corrosive; and (3) treatment or disposal of the concentrated brine by-product and other process residuals.

Pretreatment is performed to remove excessive suspended solids or other compounds that have a high membrane fouling potential. The primary objectives of pretreatment are to extend membrane life and improve or optimize system recovery, and the pretreatment processes most often used include prefiltration and chemical conditioning.[7] Prefiltration can take the form of sand, dual-media, or multi-media filtration, bag or cartridge filtration, or even coarser membrane filtration. Chemical conditioning pretreatments may include pH adjustment, disinfection, sequestering or dispersing agent addition, and chemical addition for precipitation of scaling compounds such as calcium carbonate, barium sulfate, and silica compounds.[7] The application of chemical addition for pH adjustment and precipitation of insoluble metal salts was discussed earlier in this chapter.

Post-treatment of the permeate is often required because the membrane treatment or pretreatment processes remove the buffering capacity of the water and the result is a corrosive water that can be aggressive to receiving piping, fittings, and tankage. Additionally, the membrane treatment processes do not remove dissolved gases, such as hydrogen sulfide and carbon dioxide, that add to the corrosive nature of the permeate.[7] Chemical conditioning treatment may include degasification using aeration or air-stripping processes, the addition of soda ash for increasing the alkalinity and buffering capacity of the water, or pH adjustment using caustic.

Residuals that must be managed when implementing a membrane treatment process include spent cartridges if using disposable microfiltration units; spent cleaning chemicals and backwash waters; and the concentrated brine or retentate, which generally is 15 to 25 percent of the feed water flow rate.[7] All residues must be managed in accordance with federal, state, and local regulations regarding solid and liquid waste disposal.

Options available for backwash waters and concentrates include recycling, surface-water discharge, sanitary sewer discharge, land application, deep well injection, evaporation, and crystallization.[7] Recycling the backwash and concentrate streams back into the process to further concentrate the residuals maximizes the efficiency of membrane treatment and the amount of treated water produced from each gallon of water processed. However, there will be a limit to which the residuals can be concentrated, and, ultimately, another disposal option for those residuals will be necessary.

Surface-water and sanitary sewer discharge are typically the least expensive options. Because the residuals will have high concentrations of total dissolved solids, permitting and compatibility with the receiving water will limit the areas in which these discharge options can be used. Land application must consider toxicity to plant species and bioaccumulation of metals. Deep well injection can be an effective disposal option for these concentrated waste streams, but it will be more costly than the previously discussed options. From an environmental perspective, evaporation and crystallization are the most attractive disposal options. These techniques further concentrate the dissolved solids with the intent of generating zero liquid discharge. Solids generated following evaporation or crystallization may be landfilled or possibly recovered as a recycled product.

DISTILLATION

Distillation is the evaporation and condensation of the water stream. The inorganics do not evaporate with the water and are left behind. The condensate is purified water. The process requires heating the water to increase evaporation rates and cooling of the airstream to condense the water vapor. Volatile organics will evaporate and condense with the water.

The cost of heating and cooling the water can be very expensive. However, new technology in the area has resulted in the development of multiple-effect distillation. Basically, this process uses the same energy several times in the process. Multiple-effect distillation has had broad applications on water desalination projects in the Middle East. While the technology is readily available, the cost is still relatively high for groundwater treatment.

Ion Exchange

The ion exchange properties of soil have been recognized since the 1850s. Since that time, there have been many improvements in the materials that can exchange an ion in the water for an ion on the solid-phase exchange material. The principal use of ion exchange technology today is in the softening of home potable water using synthetic resin beads.

Ion exchange is basically the exchange of an ion with a high ion exchange selectivity for an ion with a lower selectivity. Any divalent ion will usually have a higher ion exchange selectivity than a monovalent ion. Table 5-2 summarizes the selectivity for different ions on a variety of ion exchange resins. Calcium, which is divalent, will replace sodium, which is monovalent, at an exchange site on an ion exchange bed. This is the basis of water softening. The calcium ion, which increases water hardness, exchanges with the sodium ion on the ion exchange resin. The calcium is removed from the water, and the water has lost the ions that make it "hard."

The resin is regenerated by passing a high concentration of sodium ions through the ion exchange bed. All reactions go in both directions. The calcium will exchange with the sodium, but at the same time, the sodium will exchange with the calcium. The difference is that the rate of exchange for the calcium to replace the sodium is much faster than the opposite reaction. However, a high concentration of sodium ions in the water, relative to the calcium ions, will drive the exchange in the opposite direction. The ion exchange resins can be regenerated with sodium for removing further hardness from the water.

All of the heavy metals present in water are in the divalent or trivalent state, except for hexavalent chromium. A simple home sodium ion exchange unit will remove all of these compounds. However, the process is expensive, and the regeneration brine, with the heavy metals, will still have to be disposed of off-site. These two problems severely limit the use of ion exchange for large quantities of heavy metals. The best use of ion exchange is for very low concentrations and for final treatment before potable use.

Ion exchange can also be used to remove anions, negatively charged particles. Chlorides, nitrates, sulfates, etc. can be removed by anion

TABLE 5-2 Ion Exchange Resin Selectivity

Resin	Selectivity[a]
Strong acid	Li^+, H^+, Na^+, NH_4^+, K^+, Rb^+, Cs^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Pb^{2+}
Weak acid	Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, H^+
Strong base	F^-, OH^-, $H_2PO_4^-$, HCO_3^-, CI^-, NO_2^-, HSO_3^-, CN^-, Br^-, NO_3^-, HSO_4^-, I^-
Weak base	F^-, CI^-, Br^-, I^-, PO_4^{3-}, NO_3^-, CrO_4^{2-}, SO_4^{2-}, OH^-

Source: From Patterson, J.W., *Wastewater Treatment Technology*, Ann Arbos Science, Ann Arbor, MI, 1978.

[a] Increasing selectivity left to right.

exchange resins. Hexavalent chromium is, in fact, removed by anion resins. One of the emerging compounds discussed in Chapter 8, perchlorate, has been extensively treated using anionic ion exchange resins.

All ions can be removed by ion exchange. Sodium ions can be removed by ion exchange resins using hydrogen. Hydrogen ions exchange with the sodium ions in the water. Sodium has a higher exchange potential than hydrogen. Combining anion exchange resins in the hydroxide form with cation exchange resins in the hydrogen form will remove all of the ions in the water. The remaining hydrogen and hydroxide ions combine to form water.

This process is used to make ultrapure water for high-pressure boilers. The same process could be used to treat groundwater when the contaminant is dissolved solids. Once again, this is a very expensive process. Normally, an aquifer would be abandoned rather than cleaned of dissolved solids. When treatment is necessary, reverse osmosis or distillation would be the preferred method.

References

1. James M. Montgomery, Consulting Engineers, Inc., *Water Treatment Principles and Design*, Wiley, New York, 1985.
2. Steel, E.W., and McGhee, T.I., *Water Supply and Sewage*, 5th edition, McGraw-Hill, New York, 1979.
3. Conner, J. R., *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.
4. U.S. Environmental Protection Agency, *Treatment Technologies for Mercury in Soil, Waste, and Water*, EPA 542-R-07-003, August 2007.
5. Patterson, J.W., *Industrial Wastewater Treatment Technology*, 2nd edition, Butterworth, Stoneham, MA 1985.
6. Tchobanoglous, G., F.L. Burton, and H.D. Stensel, *Wastewater Engineering Treatment and Reuse*, 4th edition, McGraw-Hill, New York, 2003.
7. U.S. Environmental Protection Agency, *Membrane Filtration Guidance Manual*, EPA 815-R-06-009, November 2005.
8. Baker, R.W., *Membrane Technology and Applications*, 2nd edition, Wiley, New York, 2004.
9. Gregory, R., and P. Palmer, Nitrate removal from groundwater utilizing reverse osmosis, in *Proceedings of the National Outdoor Conference on Aquifer Restoration, Groundwater Monitoring and Geophysical Methods*, May 1990, Las Vegas, Nevada.
10. Srikanth, G., "Membrane separation processes—technology and business opportunities", *Chemical Engineering World*, Vol, 34, No. 5: 55–66, May 1999.

6

Air Treatment Technologies

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In many groundwater treatment technologies used today, organic contaminants are volatilized either in situ or in aboveground process units. Volatilization involves the transfer of the contaminants from the dissolved phase (in water) to the vapor phase (in air). The group of compounds typically treated by groundwater remediation system is referred to as Volatile Organic Compounds (VOCs), which are generally lower molecular weight organic compounds with higher vapor pressures. Generally, VOCs that require remediation originate from petroleum products either as mixed compounds, such as gasoline, or single compound sources, such as benzene or toluene. A subset of VOCs includes chlorinated VOCs, which are chlorinated petroleum products (such as trichloroethene); these are common groundwater contaminants requiring remediation. Table 6-1 lists some of the more common VOCs that are treated by vapor-phase treatment systems and are grouped according to the type of chemical(s) released.

The VOCs identified in Table 6-1 are typically toxic compounds and are also ignitable. For these reasons, VOC treatment may be necessary to minimize the impact to human health and the environment, for safety reasons, and to assure that remediation systems are in compliance with all air emission regulations and standards. It is also important to properly design and select the vapor treatment system because the cost for vapor treatment can be a significant portion of the overall cost of a groundwater remediation project. Although highly project specific, vapor treatment costs can be 20 to 60 percent of the total operations and maintenance costs for a groundwater remediation system.

Several groundwater remediation methods generate vapors and therefore require vapor treatment, including (1) in situ soil vapor extraction, (2) multiphase extraction, (3) in situ air sparging, (4) bioventing systems, and (5) ex situ groundwater treatment units, which include air strippers and air diffusers. These remediation techniques are addressed

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TABLE 6-1 Commonly Treated Volatile Organic Compounds

Most common petroleum VOCs related to gasoline, diesel, and other fuels releases and/or distributed as individual compounds
Benzene
Toluene
Ethylbenzene
Xylene
Other VOCs found in petroleum fuels and/or distributed as individual compounds
Benzyl chloride
Bromodichloromethane
Bromomethane
Carbon disulfide
Chlorobenzene
1,2-Dichlorobenzene
Chloroform
Chloromethane
Cyclohexane
Ethyl acetate
Ethylene dibromide
Isopropyl benzene
4-Methyl-2-pentanone
Methyl tertiary butyl ether
Naphthalene
Styrene
Tetrahydrofuran
Tribromomethane
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Chlorinated solvents
Dichloroethene
1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Trichloroethene
Vinyl chloride
cis-1,2-Dichloroethene
Tetrachloroethene
Methylene chloride
Methyl ethyl ketone
Carbon tetrachloride

in other chapters of this book, but in all of these techniques, the treatment of the vapors is accomplished using aboveground treatment process units.

The most common vapor treatment technologies can be classified as adsorptive, oxidative, or biological. The adsorption-based technologies include VPGAC and synthetic polymer adsorbents. Oxidative technologies include thermal oxidation and catalytic oxidation. Biological-based systems include biofilter units that are either bioreactor vessels (tanks) or in engineered soil mounds. Less commonly utilized technologies include vapor compression, UV/ozone oxidation, and refrigeration. The more commonly used technologies, adsorption, oxidation, biological, and scrubbing, are discussed in this chapter. This chapter also discusses vapor system design criteria and treatment technologies and presents a case study to highlight the presented concepts.

DESIGN CRITERIA

Because of regulatory treatment requirements and the magnitude of vapor treatment costs, the design engineer must carefully evaluate and select the most appropriate vapor treatment technology, using the following design criteria:

- Regulatory requirements
- Composition of the process vapor stream (types of compounds and concentrations)
- Overall mass of the VOCs to be treated
- Life cycle emissions estimation
- Siting considerations
- Utility availability
- Other project-specific considerations

Regulatory Requirements

The cleanup requirements or necessary removal efficiency of a vapor-phase treatment system is dictated by regulatory requirements. The federal air laws were initiated with the Clean Air Act in 1963, and additional amendments were promulgated in 1970, with the most recent amendments added in 1990. The Clean Air Act regulates criteria pollutants, such as ozone, sulfur dioxide, particulate matter, lead, nitrogen oxides, and carbon monoxide, and also regulates hazardous air pollutants. The hazardous air pollutants are the primary compounds of interest for groundwater remediation systems, and the Clean Air Act specifies 189 hazardous air pollutants in addition to various categories of air emissions.

Although the Clean Air Act regulates air emissions, the enforcement of the Clean Air Act is primarily conducted at the state level. States have developed State Implementation Plans that determine how the states will implement the Clean Air Act. Oftentimes, the state will transfer the authority and enforcement of the Clean Air Act to local county agencies. In many remediation projects across the United States, determination of emission standards and the design of vapor treatment systems are going to be determined by the state or local county environmental agencies.

Emission requirements can be quite variable and can come in several forms:

- Maximum achievable control technology, which specifies that the best available technology be used for treatment of the vapors (for example, there may be a specification that either thermal oxidizer, catalytic oxidizer, and/or vapor-phase carbon must be used for a minimum of 30 days after starting a soil vapor extraction system).
- Compound-specific mass limitations (for example, the benzene emission cannot exceed 0.5 pounds per day).
- General (or categorical) mass limitation (for example, TPH cannot exceed 10 pounds per day).
- Compound-specific concentration at the discharge point or at a target area (for example, benzene concentration must not exceed 5 parts per million by volume (ppmv) in the breathing zone). This type of requirement would be evaluated using air dispersion models to evaluate specific-site conditions and predicted concentrations in a specific area of interest.

In some cases, the regulatory authority may impose several types of requirements that could include combinations of emission requirements. For example, general or categorical mass limitation may be combined with a compound-specific limitation, such as that the emissions must not exceed 10 pounds of TPH per day and no more than 0.5 pounds of benzene per day.

There are cases in which keeping air emissions within the standards is possible by means other than treatment systems. It may be feasible to meet the air emission standards by limiting the operation of the remediation systems. For example, if the air emission rates can be met by operating the remediation system for 12 hours per day rather than 24 hours per day, this may be an alternative to avoid vapor-phase treatment. In this example, the remediation time for the project may be extended, and a detailed cost analysis is required to determine if overall project costs can be reduced. In some cases, vapor emissions from remediation sites may be temporary sources of discharge, and the short duration of the emission may exempt its permitting and control in some areas.

Composition of Vapor Process Stream

To determine regulatory compliance as discussed above, it is important to understand the types of compounds and the concentrations of the vapors being emitted from the remediation process units. An understanding of the type and magnitude of the vapor stream is determined in the initial phase of the remediation project, in the site investigation phase. The investigation work provides the basic understanding of the site and presents the description of the contaminant impacts, including (1) type of contaminants, (2) magnitude of the contaminant concentrations, and (3) delineation or size of the impacted area. This information provides the basis for the selection of the remediation method used for the site.

If the selected remediation method is an air stripper or air diffuser that volatilizes VOCs from groundwater in an aboveground treatment unit, no additional data collection may be needed since the composition of the vapor stream from the air stripper or air diffuser can be estimated with good accuracy. The VOC concentration and mass flow rate can be estimated by using the (1) design pumping rate of the groundwater recovery system, (2) the air-to-water ratio of the air stripper or diffuser, and the (3) contaminant types and concentrations in the groundwater within the pumping radius of the groundwater recovery system. This process is illustrated in Example 6-1.

EXAMPLE 6-1

A pump-and-treat system is designed to remediate a groundwater plume impacted with trichloroethene. From investigation data and the analysis of the plume, the trichloroethene concentrations are expected to be 2,500 μg/L when the system is started. From groundwater modeling, the groundwater recovery flow rate is designed to be 40 gpm. A low-profile air stripper has been selected to treat the recovered groundwater. The results of the air-stripper modeling indicate that 300 cubic feet per minute (cfm) of air is required to properly strip the groundwater at a temperature of 16°C, resulting in a 99.8-percent removal of the trichloroethene. Determine the expected vapor mass loadings (pounds per day [lbs/day]) and vapor concentrations (mass basis and volume basis) that will provide the design basis for the vapor treatment system.

Solution

Step 1–Determine the expected vapor mass loadings in lbs/day

- Assume that 100 percent of the trichloroethene is transferred from the groundwater to the vapor phase
- Use a standard conversion factor to determine the mass in groundwater:

$$\begin{aligned}\text{Mass in lbs/day} &= \text{concentration (mg/L)}\\ &\quad \times \text{water volume processed (mgd)} \times 8.34\end{aligned}$$

$$\text{mgd} = \text{million gallons per day}$$

40 gpm = 0.0576 mgd

trichloroethene mass (lbs/day) =

$$\left(2.5\frac{\text{mg}}{\text{L}}\right) \times (0.0576\ \text{mgd}) \times 8.34 = 1.2\ \frac{\text{lbs}}{\text{day}}\ \text{trichloroethene}$$

(as noted above, all the mass will be transferred to the vapor phase)

Step 2–Determine the trichloroethene concentration in the vapor stream on a mass basis

- Mass basis for vapors is commonly expressed as milligrams per cubic meter(mg/m^3).
- Determine the density of the trichloroethene in the vapors (mass/volume):

$$\left(\frac{1.2\ \frac{\text{lbs}}{\text{day}}}{300\ \frac{\text{ft}^3}{\text{min}}}\right) \times \left(\frac{1\ \text{day}}{1{,}440\,\text{min}}\right) \times \left(\frac{35.31\,\text{ft}^3}{1\,\text{m}^3}\right) \times \left(\frac{453{,}590\,\text{mg}}{1\,\text{lb}}\right) = 44.5\ \frac{\text{mg}}{\text{m}^3}$$

Step 3–Determine the trichloroethene concentration in the vapor stream on a volume basis

- Mass basis for vapors is commonly expressed as parts per million by volume (ppmv).
- Convert the concentration from step 2 to units in ppmv:

$$\text{ppmv} = \frac{\text{mg/m}^3 \times (273.15 + T_c)}{12.187 \times \text{MW}}$$

$$T_c = \text{vapor temperature } (^\circ\text{C})$$

$$\text{MW} = \text{molecular weight}$$

$$\text{ppmv} = \frac{(44.5\,\text{mg/m}^3) \times (273.15 + T_c)}{12.187 \times 131.4}$$

$$= 8.0\ \text{ppmv}$$

If other remediation methods are recommended, such as soil vapor extraction, determining the vapor composition of the off-gases may not be simple. In this case, the most effective method for determining the vapor composition is by performing a short-term pilot test in the treatment area. The methodology of performing pilot tests is not discussed in full here, but is discussed in general terms.

In the pilot test, vapors should be extracted from the treatment area using equipment that is similar to the full-scale treatment system (i.e., achieving similar airflow rates and vacuum rates). For a soil vapor extraction pilot test, the test may include the installation of a single test well that is screened within the vadose zone. A vacuum blower would be used to create a vacuum and extract soil vapors. The VOCs in the extracted vapors may be measured over time (1 to 8 hours) to understand how the VOC concentrations change over time. Also, soil vapors should be collected and analyzed in a laboratory. This analytical data will provide the VOC types and concentrations needed for the design of the vapor treatment system.

The results of the pilot test are scaled up to simulate the full scale. For example, if the full-scale system is designed to have 20 wells, then the air flow data from the single well pilot test needs to be multiplied by 20. This simplistic approach is sufficient for evaluating and sizing the air-phase treatment system; however, there may be interactions between extraction wells in the full-scale system that may not be completely simulated in the pilot test. The full-scale flow rates (on a per well basis) may be less than those observed in the pilot test.

An example of using pilot test data to estimate the full-scale vapor composition is provided in Example 6-2.

EXAMPLE 6-2

A soil vapor extraction pilot test was performed at a site impacted with benzene. The pilot test included one test extraction well located within the impacted area. The pilot test results indicated that an extraction airflow rate of 20 cfm produced sufficient vacuum conditions in the vadose zone. An air sample was collected during the test, and the benzene concentration was 350 ppmv (at a temperature of 20°C). The design of the full-scale system includes 10 soil vapor extraction wells across the impacted area. Determine the vapor concentrations (volume basis and mass basis) and expected vapor mass loadings (lbs/day) that will provide the design basis for the full-scale vapor treatment system.

Solution

Step 1–Determine the expected benzene concentration in the vapor stream on a volume basis (ppmv)

The pilot test indicated that the vapor concentration (by volume) was 350 ppmv. This concentration is assumed to be representative of the impacted area and is the concentration for the full-scale system.

Step 2–Determine the expected benzene concentration in the vapor stream on a mass basis (mg/m³)

$$\frac{\text{mg}}{\text{m}^3} = \frac{\text{ppmv} \times 12.187 \times \text{MW}}{273.15 \times T_\text{C}}$$

$$\begin{aligned}&\text{Molecular weight for benzene} = 78.1\\ &= \frac{(350\,\text{ppmv}) \times 12.187 \times 78.1}{273.15 + 20}\\ &= 1{,}136\ \frac{\text{mg}}{\text{m}^3}\end{aligned}$$

Step 3–Determine the vapor mass loading in lbs/day to the vapor-phase treatment system

- The pilot test well airflow rate was 20 cfm
- Ten wells are included in the full-scale design
- Therefore, 10 wells × 20 cfm/well = 200 cfm for the system:

$$\text{Mass loading}\left(\frac{\text{lbs}}{\text{day}}\right) = \text{airflow rate}\left(\frac{\text{ft}^3}{\text{min}}\right) \times \text{concentration}\left(\frac{\text{mg}}{\text{m}^3}\right) \times \text{CF}$$

CF = conversion factors

$$\begin{aligned}&= 200\frac{\text{ft}^3}{\text{min}} \times 1{,}136\frac{\text{mg}}{\text{m}^3} \times \frac{1{,}440\,\text{min}}{\text{day}} \times \frac{1\,\text{m}^3}{35.31\,\text{ft}^3} \times \frac{1\,\text{lb}}{453{,}600\,\text{mg}}\\ &= 20.4\frac{\text{lbs}}{\text{day}}\end{aligned}$$

In both examples discussed above, it is important to note that the vapor composition may change over time. In both cases, air stripper and soil vapor extraction, the VOCs will generally decline over the length of the groundwater remediation project. In most cases, the estimated vapor concentrations at start-up represent the worst-case or highest concentrations. In a groundwater recovery system (using an air stripper for treatment), the VOC concentrations in the off-gases may decline very slowly over the course of many years. In a soil vapor extraction, the decline in VOC concentrations is typically much more dramatic, and significant decreases can be observed over just a few months. Once again, life cycle design should be considered when developing the long-term vapor-phase treatment system.

Overall Mass of Contaminants to Be Treated

An estimation of the total mass of VOCs that may be recovered by the remediation system is often needed to evaluate the appropriate treatment technology and overall project costs. This is particularly true for adsorbent-based treatment systems such as GAC or synthetic polymer adsorbents. For example, let's assume that a gasoline release occurred, and 1,000 pounds of gasoline are known to be in the subsurface. From this, it is estimated that 65 percent of the mass will be recovered by the soil vapor extraction system (650 pounds), 30 percent will be biodegraded (300 pounds), and 5 percent (50 pounds) will not be recovered (ratios are based on empirical projection). The expected amount of GAC can be estimated assuming that GAC has a weight adsorption capacity of 7 percent (that is, 100 pounds of GAC can adsorb 7 pounds of gasoline compounds). The amount of GAC required to treat the vapor stream is estimated to be 9,300 pounds. The cost of other technologies can also be estimated based on the mass of VOCs.

Several methods can be used to estimate the mass of VOCs in the subsurface, and are usually performed in the investigative stages of the remediation project. Although not fully discussed in this book, the contaminant mass calculations are based on (1) an estimation of the volume of contaminated media (soils, groundwater, and data on the location of any free-phase product); (2) the analytical data of the contaminated media (soil analytical data, groundwater analytical data, and free-phase product data); and (3) the physical data on the contaminated media that may include soil composition, unit weight, organic composition, total and effective porosity, and other site-specific data. Most of these data can be incorporated into simple models or much more complex three-dimensional models for estimating the total mass at the site.

When the overall mass estimate calculation is completed, an estimate can be made of the amount or percentage that is expected to be extracted and treated by the remediation system. The remediation engineer can make projections about the recovery times of the contaminants and develop a typical contaminant mass recovery curve as shown in Figure 6-1. These data are very useful for the selection of vapor-phase treatment equipment and the project life cycle design discussed below. However, it is important to note that calculations and estimates of contaminant mass are difficult and many times not very accurate (i.e., they generally reflect a lower mass than actually exists). This observation should be taken into account when designing the life cycle design and cost estimates for the vapor-phase treatment system.

Life Cycle Emission Concentration

The design of remediation systems should always include a life cycle analysis, which includes an evaluation of the effectiveness and cost of

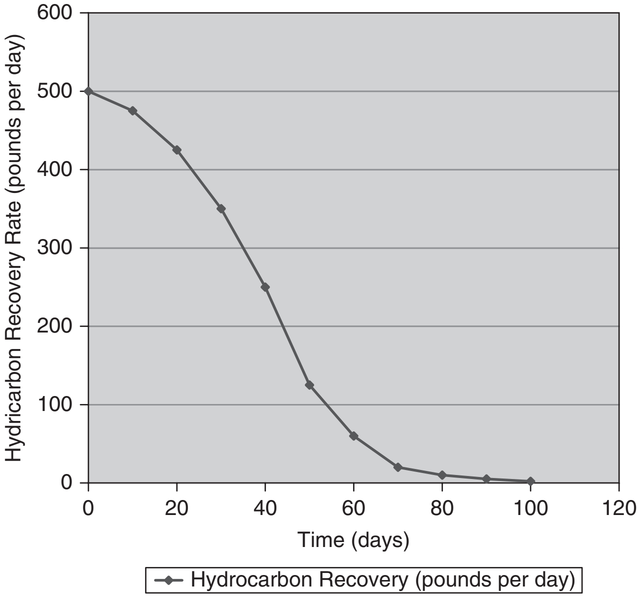


FIGURE 6-1. Typical contaminant mass recovery curve.

treatment system from start-up through the end of the project when contaminant concentrations are significantly reduced. This is particularly true for the treatment of vapor emissions, where concentrations may drop four orders of magnitude over a project lifetime. Emission control technology selection is more significantly affected by concentration than volume throughput for vapor-phase treatment than for liquid-phase treatment. For example on a groundwater treatment design, an air stripper will generally be chosen for the treatment of 100 µg/L or 100 mg/L of groundwater contaminated by BTEX compounds. This choice will be made for almost any flow rate. On the other hand, an emission stream of 10,000 ppmv vapors from a soil vapor extraction system (300 cfm) is best treated by a thermal oxidizer. As the concentrations drop to 1,000 ppmv, the vapors are best treated by catalytic oxidation. As the concentrations continue to drop to 20 ppmv, the optimal choice may be GAC.

The design of the remediation system should incorporate all the anticipated life cycle changes and be installed with sufficient flexibility for future modifications or changes in treatment methods. For example, at a site where soil vapor extraction emissions are expected to be above 300 ppm for six months and then drop off rapidly (typical small service station, limited spill situation), a catalytic oxidizer may be rented for the first six months, and subsequently, GAC may be installed at the site for the remainder of the project. Space, utility availability/connections, and permitting must all be incorporated into the design of the system. Regarding permitting, the anticipated changes in vapor-phase treatment systems can be included in remedial action design documents to allow for preapproval of the various vapor-phase equipment that may be used throughout the project. This can be advantageous to keep the remediation progress moving forward and minimizing any regulatory approval time delays when changing the vapor-phase treatment equipment.

The primary information that is necessary to prepare a life cycle design is the contaminant mass recovery curve and costs for various treatment methods. The contaminant mass recovery curve is discussed in the section above. Developing cost estimates for various technologies must be completed by the design engineer, and there are several factors that will affect the cost of the systems, including vapor flow rate, contaminant mass loading and concentration, vapor moisture conditions, local utility rates (electricity, natural gas, propane), and availability of carbon regeneration/disposal facilities. A typical cost analysis table is shown in Table 6-2 and compares costs for GAC and catalytic oxidation treatment.

Siting and Utility Considerations

There are several siting considerations that need to be evaluated prior to treatment technology selection. Some of these constraints include availability of utilities, utility costs, issues related to operation and maintenance, aesthetic issues, local land use (industrial, commercial, and residential), and buffer areas.

The availability of utilities and their ability to accommodate the treatment equipment must be carefully evaluated. Electrical power must be available in the appropriate phase and voltage to power the equipment. Some difficulties may arise with thermal and catalytic oxidation systems because they may require supplemental fuel sources (natural gas or propane) that may not be readily available. When available, using natural gas from local distribution systems tends to be the lowest cost option, but natural gas piping distribution systems are not available in all areas. Also, the local natural gas distribution system must have sufficient pressure and volume for the oxidizer selected. High-pressure natural gas line connections to the oxidizer typically require additional lead time for permitting and installation. In some areas, natural gas may not be an option, and propane must be used for oxidizers. Propane is more expensive than natural gas (generally one

TABLE 6-2 Cost Analysis for Vapor Treatment Costs

	GAC				Catalytic Oxidation (electric)			
Influent[a] Concentration (ppmv)	VOC Loading (pounds/ day)	Adsorption Rate (%)	GAC Usage (pounds/ day)	Cost[b] ($/day)	Electric Usage (kw-hrs)	Electric Cost ($/day)	Cost[c] ($/day)	Comments
50	1.5	8.2	18	$106	11.0	23.04	$213	
100	2.9	10.4	28	$169	10.0	22.56	$213	Similar cost at approximately 145 ppmv <145 ppmv, GAC is more cost effective >145 ppmv, catalytic oxidation is more cost effective
200	5.8	12.9	45	$271	10.0	21.84	$212	
500	14.6	17.2	85	$509	9.0	19.68	$210	
1000	29.2	21.2	138	$826	7.0	16.08	$206	
2000	58.3	26.0	224	$1,343	4.0	9.12	$199	
3000	87.5	29.4	297	$1,783	1.0	2.16	$192	

[a] *Operation conditions*: airflow rate = 100 scfm, (70°F) = 106 acfm (100°F); benzene is the only VOC; 1 ppmv = 3.06 mg/cubic meter (benzene); vapor temperature = 38°C (100°F); relative humidity = 50%.

[b] *Carbon costs*: $6 per pound (includes new carbon, vessel rental, changeout, and regeneration).

[c] *Catalytic costs*: costs include rental and fuel consumption; electricity cost = $0.09 kWh; unit costs = $4,000 per month ($135 per day) + $3,000 mobilization/demobilization + $2,000 start-up services; mobilization/demobilization and start-up costs averaged over 3 months = $5,000 per 90 days = $55 per day, total daily rate = $190 per day.

and one-half to two times higher than natural gas) and presents other installation and operational considerations. Sufficient space needs to be available for spotting on-site propane tanks and the area required for the refilling of the tanks using propane tanker trucks. Also, there may some logistical problems associated with frequent fuel deliveries. The design engineer needs to conduct a thorough evaluation of fuel source availability and costs and choose the most appropriate power source for powering the treatment unit.

Contaminant releases and the locations of remediation systems can be in industrial areas, commercial areas, and sometimes adjacent to residential areas. The design engineer must take into account the local environment in which the system will be situated. Vapor treatment systems involve stack discharges that may cause some odors, which may be problematic in residential areas. Also, vapor emissions from oxidizers can be very hot ($>1{,}400^{\circ}$F), and the stacks must be situated so they do not affect any surrounding equipment or facilities. Although vapor treatment systems are designed to treat vapors and prevent them from being discharged to the atmosphere, it may be possible that high concentration vapors are emitted during system start-up or at unexpected times associated with an upset condition of the treatment system. Although controls should be in place to prevent any unintentional release of untreated vapors, the potential may exist. It is advisable to be aware of any ignition sources near the equipment and especially the stack, including electric wires, cars, trucks, welding equipment, and unrated electrical panels. Buffer areas around equipment and stacks should be provided to limit the potential of exposure to hazardous vapors and potential explosive conditions.

TREATMENT TECHNOLOGIES

Adsorption-based Treatment Technologies

Adsorption is a process by which material accumulates on the interface between two phases. In the case of vapor-phase adsorption, the accumulation occurs at the air/solid interface. The adsorbing phase is called the adsorbent, and the substance being adsorbed is termed an adsorbate. It is useful to distinguish between physical adsorption, which involves only relatively weak intramolecular bonds, and chemisorption, which involves essentially the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Physical adsorption requires less heat of activation than chemisorption and tends to be more reversible (easier regeneration).

GAC is the most popular vapor-phase adsorbent in the remediation industry. A number of new synthetic resins, however, have shown increased reversibility and have higher adsorption capacities for certain compounds.

The most efficient arrangement for conducting adsorption operations is the columnar continuous plug-flow configuration known as a fixed bed. In this mode, the reactor consists of a packed bed of adsorbent through which the vapor stream is passed. As the airstream travels through the bed, adsorption takes place, and the effluent is purified. A typical concentration profile along an adsorbent column is shown in Figure 6-2.

The part of the adsorption bed that displays the concentration gradient is termed the mass transfer zone. The amount of adsorbate within the bed changes with time as more mass is introduced to the adsorbent bed. As the saturated (spent or used) zone of the bed increases, the mass transfer zone travels downward and eventually exits the bed. This gives rise to the typical effluent concentration versus time profile, called the breakthrough curve (Figure 6-3). The reader is referred to several textbooks for adsorption theory, multicomponent effects, isotherm description, and modeling.[1] This basic knowledge of adsorption theory is critical to proper understanding and selection of the various adsorbents.

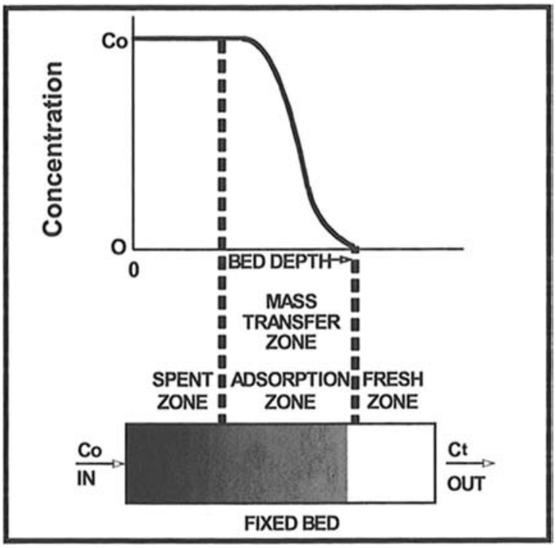


FIGURE 6-2. Typical concentration profile along an adsorbent column. (Adapted from Noll et al.[1])

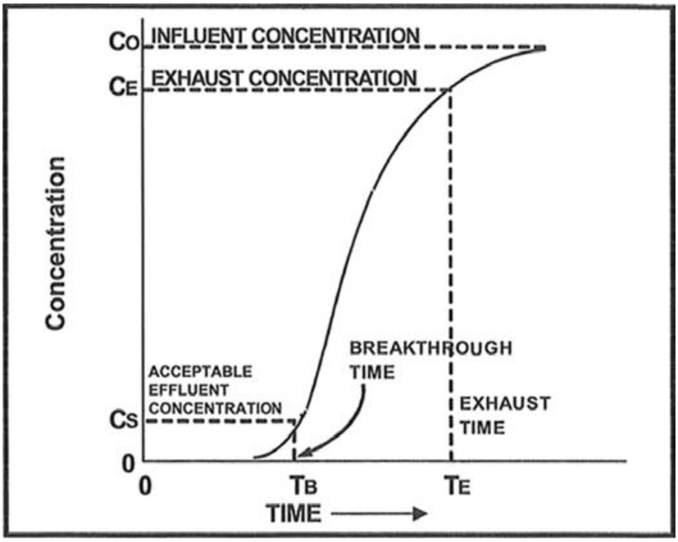


FIGURE 6-3. Breakthrough curve for a typical adsorber column. (Adapted from Noll et al.[1])

Off-site Regenerable/Disposable Vapor-phase Granular Activated Carbon

Vapor-phase GAC is an excellent adsorbent for many VOCs commonly encountered in soil vapor extraction, air sparging, vacuum-enhanced recovery, and air-stripper vapor treatment applications. The adsorption capacity of GAC is often quantified as the mass of contaminant that is adsorbed per pound of GAC. This nominal adsorption capacity is a useful guide for pure compound adsorption but can be misleading when complex mixtures of VOCs are treated. Breakthrough, or GAC bed life, is observed when the compound most difficult to adsorb breaches the filter. Isotherm data (milligrams adsorbate removed per gram adsorbent at a constant temperature) and other product-specific data are generally available for contaminants of interest from carbon vendors, as well as in the published literature. Pilot testing for GAC feasibility is rarely conducted, except in instances where complex mixtures of VOCs are encountered.

GAC is generally a good adsorbent for hydrocarbon-based VOCs and some chlorinated VOCs. GAC has limited adsorption capacity for ketones and generally poor adsorption of volatile alcohols. Table 6-3 presents typical adsorption removal efficiencies for a variety of VOCs by GAC under constant temperature and moisture conditions (as stated in the table).

TABLE 6-3 Granular Activated Carbon Adsorption Capacity for Some Common Volatile Organic Compounds

	GAC Capacity (pounds of VOCs per 100 pounds of GAC)[a]				
VOC Concentration	10 ppmv	50 ppmv	100 ppmv	200 ppmv	500 ppmv
Benzene	6.77	11.21	21.19	34.76	21.60
Toluene	14.02	20.52	24.09	28.29	35.10
Ethylbenzene	22.40	30.26	34.49	39.39	44.92
Xylene	22.75	30.76	35.07	40.08	43.77
Methyl tertiary butyl ether	5.68	9.16	11.06	13.24	16.59
Naphthalene	58.94	60.38	60.65	60.71	60.72
1,1-Dichloroethene	1.39	3.35	4.72	6.50	9.66
cis-1,2-Dichloroethene	2.73	6.15	8.45	11.50	16.54
trans-1,2-Dichloroethene	1.96	4.55	6.32	8.59	12.56
1,2-Dichloroethane	4.63	9.27	12.14	15.62	21.36
1,1,1-Trichloroethane	10.12	16.81	20.60	25.06	32.19
Trichloroethene	11.20	18.79	23.15	28.33	36.82
Vinyl chloride	0.03	0.15	0.28	0.52	1.12
Tetrachloroethene	29.19	42.79	50.38	59.36	74.05
Methylene chloride	0.36	1.31	2.16	3.46	6.15
Methyl ethyl ketone	2.60	5.27	6.64	8.19	10.50

Source: Carbonair.

[a] Carbon capacities are based on vapor temperature of 70°F, relative humidity of 50%, and 1 atm.

Note. Values adjusted to reflect usage per 100 pounds of carbon.

GAC adsorption capacity can be significantly affected by relative humidity and high temperatures. Because GAC can adsorb water in the same manner it adsorbs VOCs, water droplets and water vapor in the process airstream can significantly reduce the adsorption capacity of the carbon and cause premature breakthrough. The adsorption capacity for benzene was plotted against relative humidity and is presented in Figure 6-4. This figure shows that the optimal relative humidity should be kept below 50 percent. As the humidity increases above 50 or 60 percent, there is a significant reduction in the adsorption capacity.

The adsorption capacity may be as much as ten times higher for a low-humidity stream than for a humid airstream. This is particularly true for lower concentrations of VOCs. The humidity effects are less pronounced at higher VOC concentrations (Figure 6-5).

Humidity can be controlled by heating the air. Psychrometric charts can be used to determine the temperature rise needed to reduce the relative humidity to acceptable levels. A simplified chart is presented as Table 6-4, showing the temperature increases needed to change the relative humidity to 50 percent.

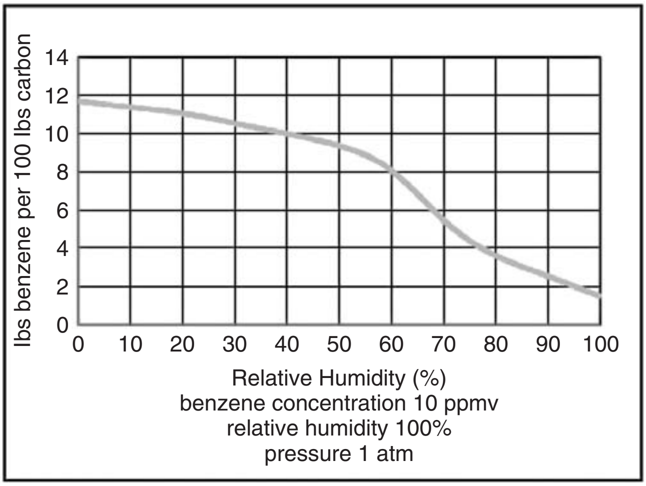


FIGURE 6-4. Effect of relative humidity on benzene adsorption capacity. (Figure provided by Carbonair.)

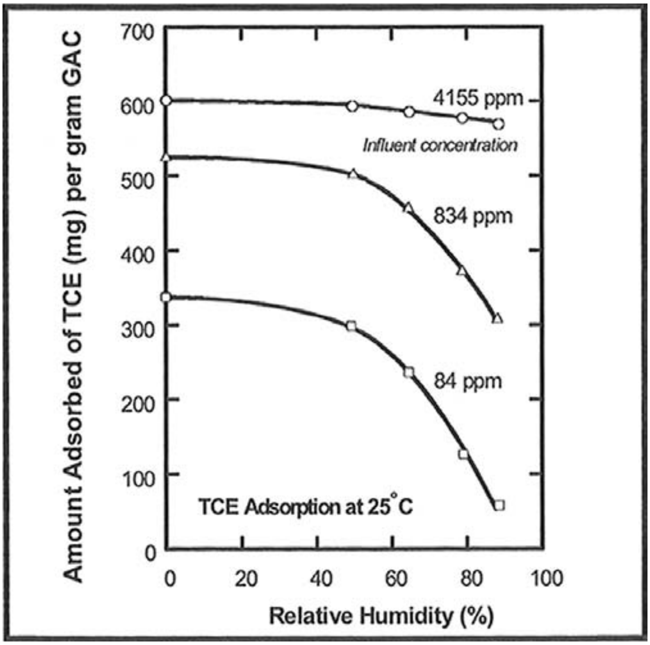


FIGURE 6-5. Effects of relative humidity on trichloroethene adsorption by granular activated carbon.

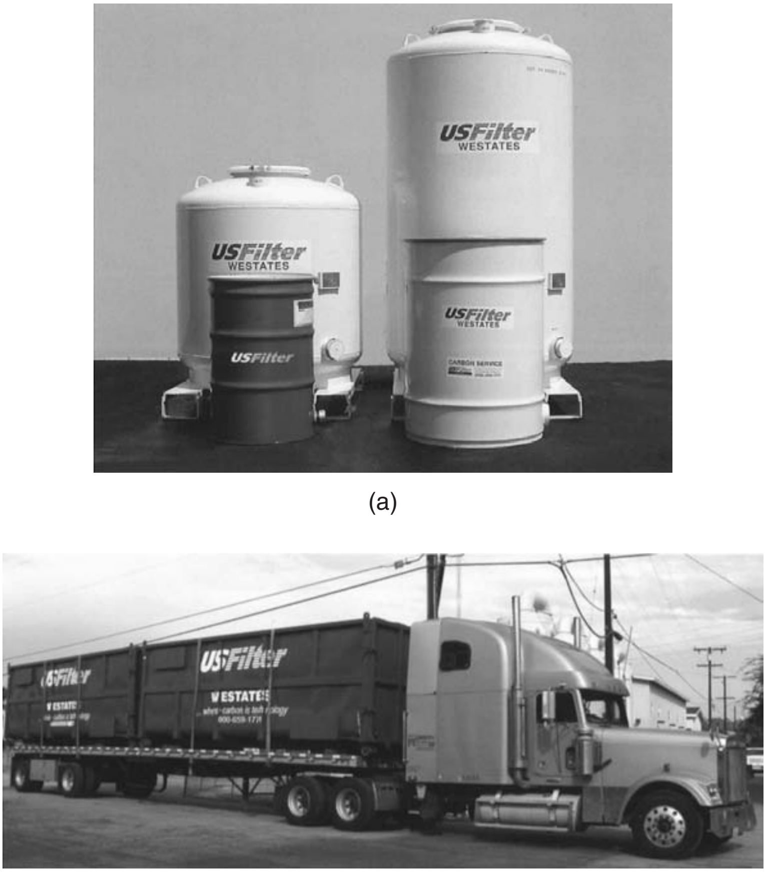
TABLE 6-4 Heating Vapors to Reduce the Relative Humidity

Temperature of Vapors at 100% Relative Humidity (°F)	Temperature Required to Reduce to 50% Humidity (°F)	Temperature Difference Required to Achieve 50% Relative Humidity (°F)
45	54	9
50	60	10
55	66	11
60	72	12
65	78	13
70	84	14
75	90	15
80	96	16
85	102	17
90	103	13
95	104	9

Note. Data determined using a psychrometric chart.

High temperatures can also reduce the GAC adsorption capacity. It is generally recommended to keep the GAC vapor inlet temperature below 100°F. Temperatures above 100°F tend to desorb the VOCs from the carbon. There are several options to control both relative humidity and temperature of vapors in remediation systems. With soil vapor extraction systems, moisture knockout tanks are used to eliminate entrained water droplets in the extracted soil vapors. In many cases with soil vapor extraction systems, the vacuum blower will provide a sufficient temperature increase to reduce the relative humidity; however, excessive temperature increases can occur across the blower. The temperature rise across the blower should be evaluated during the design and during operation to assure that the proper relative humidity and temperatures are achieved to maximize GAC adsorption. Low-profile air strippers can also use the blower to increase the temperature of the air-stripper off-gases when the blower is installed in the induced draft mode (that is, the blower pulls the air through the air stripper). Other equipment can be used to control the relative humidity and temperature, including demister elements and various types of heat exchangers. It should be noted that the adsorption vessels must also be kept warm so as to avoid water condensation on the GAC and for the airstream to maintain the proper relative humidity. GAC vessels placed outdoors in the winter on a cold day can be susceptible to condensation occurring within the vessel, which will decrease the adsorption capacity of the carbon.

The use of off-site regenerable/disposable GAC for emissions control is often limited to instances in which the mass loading is low, and, therefore, GAC consumption is low. As a general guideline, adsorption capacities for absorbable VOCs are in the 2- to 20-percent range by weight. GAC costs are approximately \$3.00 per pound (if purchased in canisters) and \$1.50 per pound for just the carbon. Cost for carbon changeout (i.e., removal of carbon from the vessel) is approximately \$1.50 per pound, and off-site regeneration or disposal is estimated to be \$1.00 to \$2.00 per pound, depending on the distance to the regeneration facilities or disposal sites. GAC can be purchased in many sizes, from a 200-pound unit (55-gallon drum) to 13,500-pound units (rectangular tanks), see Figure 6-6. Vessels are most commonly used in series to allow for effluent stream sampling between vessels to more accurately predict breakthrough times. Single vessels may also be used



(a)

(b)

FIGURE 6-6. Various granular activated carbon vessels. (Photographs provided by U.S. Filter.)

in conjunction with vapor effluent detectors that can shut down the system or switch spent vessels to stand-by unused vessels. GAC vessel/blower selection must account for head losses through the carbon system to ensure that the desired airflow is maintained.

On-site Regenerable Vapor-phase Granular Activated Carbon

Liquid-phase GAC is difficult to regenerate at low temperatures because of the adsorption of background metals and TOC (typically naturally occurring humic and fulvic acids). In the vapor phase, the GAC does not see the metals or the nonvolatile TOC and is therefore amenable to on-site regeneration. Air emission control using steam-regenerable GAC generally utilizes a two-bed system whereby one bed is on-line while the second bed is either being regenerated or in a stand-by mode. Regeneration is accomplished by passing low-pressure steam through the carbon vessel, which desorbs the contaminants (as a result of the raised temperature). The contaminated steam is subsequently cooled and is condensed. The condensed organics generally require disposal, whereas the contaminated steam may undergo water treatment (especially if a groundwater treatment system exists on-site) or may also require off-site disposal. If the condensed steam is treated on-site, it should be metered into the groundwater treatment system because the condensed steam is generally much more contaminated than the groundwater.

If regenerable systems are used for the adsorption of chlorinated VOCs, the vessels should be lined or made of an acid-resistant material. The adsorption/regeneration cycle results in the formation of some hydrochloric acid within the vessels. The hydrochloric acid formation will reduce the pH of the condensed steam.

Regenerable GAC units are also available with nitrogen regeneration. This is particularly useful to minimize steam disposal and eliminate problems with hydrochloric acid formation during steam regeneration. Regenerable beds will usually have a performance lifetime because adsorption capacity tends to diminish with continued regeneration (decay typically occurs at 70 percent of the original capacity). System lifetime ranges are dependent on the frequency of regeneration but are typically in the 3- to 7-year range. Regeneration can be conducted (1) manually during site visits, (2) by a timer system that starts up the boiler/regeneration prior to the time of expected breakthrough, or (3) using an effluent detector system (typically either a flame ionization or photoionization detector), which initiates vessel exchange and the regeneration cycle based on breakthrough.

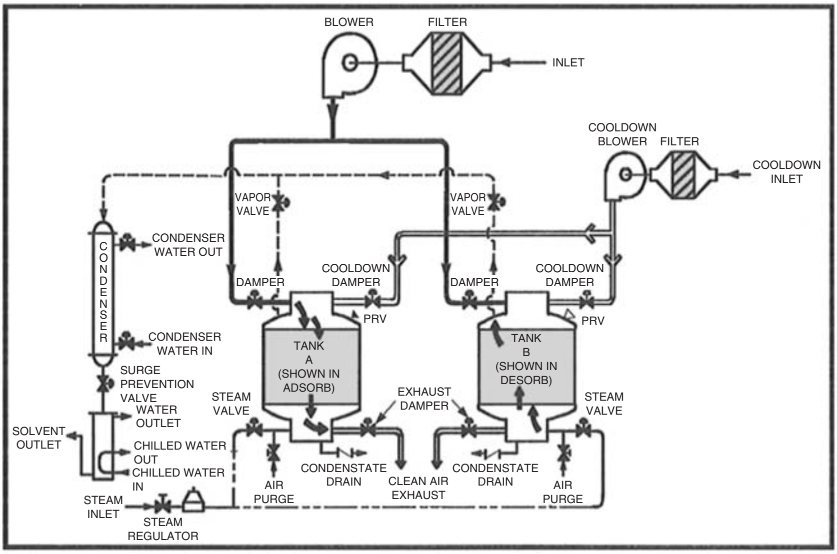


FIGURE 6-7. Regenerable granular activated carbon system schematic. (Adapted from Westport Environmental Systems.)

After completion of the regeneration, the vessel will usually undergo a drying cycle to prepare the vessel for the next adsorption cycle. Figure 6-7 provides a schematic of a regenerable GAC system. Figure 6-8 is photograph of a commercially available system.

The regeneration capability of the GAC allows for the treatment of more contaminated airstreams than is practical with off-site regenerable GAC. In soil vapor extraction applications, regenerable GAC systems are best suited for high-flow applications with moderate VOC loadings. It can be used for the treatment of halogenated and nonhalogenated airstreams. During the adsorption of highly oxidizable VOCs (ketones) in the presence of ozone or other oxidizing agents, the GAC bed may be prone to bed fires. Fire detection and suppression systems may be considered under these circumstances.

As a general guideline, a fully automated 500-cfm dual-bed GAC regeneration system may be purchased for roughly $100,000 plus an additional $10,000 for a steam unit.

Synthetic Polymer Adsorbents

Synthetic polymer adsorbent packing has been developed to overcome some of the deficiencies of GAC. The synthetic adsorbents can be plastics, polyesters, polyethers, or rubbers.[3] Polymer adsorbent systems operate very similarly to GAC systems and can be regenerated on-site

FIGURE 6-8. Regenerable granular activated carbon system. (Photograph provided by MK Environmental Inc.)

or off-site, but they are not typically used once and disposed of because of their high cost. On-site regeneration is the most typical application for synthetic polymers. Synthetic polymers have several advantages over GAC:

- They are not as sensitive to humidity as GAC; because they can be hydrophobic, they adsorb a small amount of water.
- They typically have higher adsorption rates, thus requiring less frequent changeout or regeneration.
- They are less subject to fire at higher loading rates.
- They produce less acid when used for chlorinated VOCs.
- They can be regenerated more easily because they desorb more readily and at lower temperatures using hot air or steam.
- They do not lose as much adsorption capacity following regeneration as GAC.
- They are applicable to a wider range of VOCs, including freons, aldehydes, ketones, and alcohols,[3] because of the hydrophobic nature of some types of polymers.

Although synthetic polymers offer several advantages over GAC, the cost can be more than twenty times the cost of GAC (for example, DOWEX OPTIPORE medium is $45 per pound). This cost differential has been the primary reason why synthetic polymer application has been limited in the remediation industry. Given the high cost of the polymer medium and the better ability to regenerate the medium, on-site regeneration can be a viable application for synthetic polymers. In general, the resin adsorption technology is not considered competitive for hydrocarbons because these compounds can be more economically destroyed by catalytic or thermal oxidation. The resin technology is most applicable for moderately contaminated chlorinated VOC vapor streams.

Oxidation-based Technologies

Oxidation-based technologies cause the VOCs to react at an elevated temperature with oxygen for a sufficient time to initiate the oxidation reactions. The ultimate goal of any combustion/oxidation reaction is the conversion of the VOCs to carbon dioxide, water, sulfur dioxide, and nitrogen dioxide (end products of combustion). The mechanism involves rapid chain reactions that vary with the different VOCs being oxidized. The sequential reactions leading to combustion are generally not detrimental to the environment or to the oxidative equipment unless they are interrupted (possibly insufficient residence time; or decayed catalysts). If the oxidation reactions are incomplete, partial oxidation by-products will be released in the stack effluent. Sometimes these compounds may be more noxious than the parent compound. For example, oxidation of oxygenated organics may form carbon monoxide under unsatisfactory combustion conditions. To minimize such occurrences, excess air (above stoichiometric conditions) is used during oxidation reactions. The continuity of any oxidation reaction depends on maintaining the reaction mixture (air, VOCs, temperature, and catalyst if used) in the optimal mixture range.[4] The two most common oxidation methods in the remediation industry are thermal oxidation and catalytic oxidation. A conceptual schematic of a thermal and catalytic oxidizer is shown in Figure 6-9.

Thermal Oxidation/Incineration

This technology burns the VOCs at an elevated temperature, typically in the range of 1,400 to 1,500°F, with typical residence times of 0.75 to 2.0 seconds. The burner chamber must be designed so that the VOCs pass directly through its flame, thus minimizing the possibility

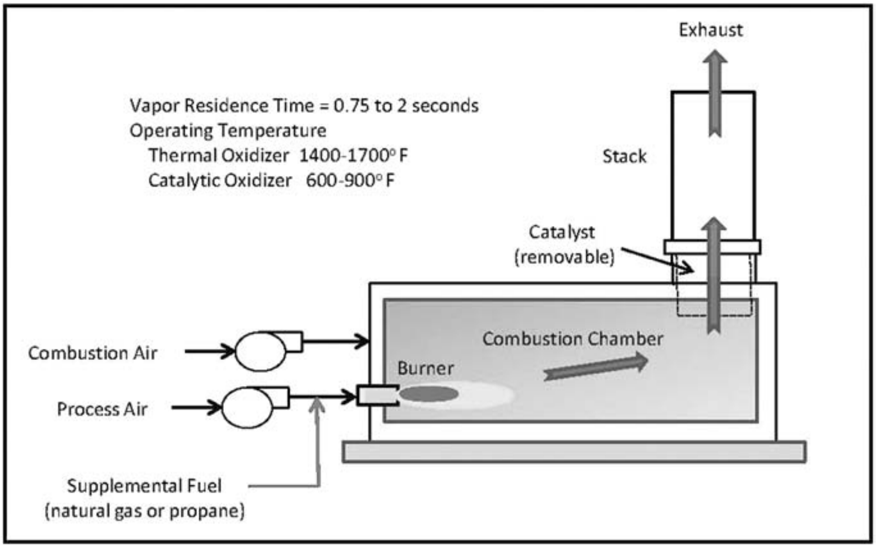


FIGURE 6-9. Conceptual schematic of a thermal and catalytic oxidizer.

of incomplete combustion. Although thermal oxidation is often the most expensive combustion-based control process, it is very well suited for high-concentration VOC airstreams (2,000- to 10,000-ppm range). Operating costs can be offset to some extent if the gas stream is already considerably above ambient temperature by utilizing the combustion heat for preheating the airstream (heat recovery). The use of this technology for airstreams that have a significant British thermal unit (BTU) value also reduces fuel consumption. VOC destruction efficiencies of well-operated thermal oxidizers are generally in the 95- to 99-percent range. Thermal oxidizers generally have a maximum allowable concentration of influent VOCs (50 percent of the lower explosive limit or in the range of 7,000 ppm [by weight]) for most hydrocarbon applications. While it is technically possible to operate thermal oxidizers above the 50-percent lower explosive limit range, the increased temperature created by oxidation of the process streams with concentrations higher than this will often exceed the temperature design criteria for most commercially available oxidizers (typically 1,600 to 1,700°F maximum.) Dilution air can be added for cooling purposes and to provide additional oxygen. During setup and operation, care must be taken to ensure that the free oxygen in the exhaust stream is maintained at a minimum of 10 percent. At some soil vapor extraction sites, subsurface zones may have limited oxygen concentrations,

FIGURE 6-10. Large gas-fired thermal/catalytic oxidizer. (Photograph provided by Intellishare Environmental, Inc.)

resulting in less than optimal destruction efficiency in the oxidizer. Figure 6-10 shows a photograph of a large thermal oxidation unit that can be modified to operate in catalytic mode by adding a catalyst bed and modifying operating set points.

The oxidation of chlorinated VOCs may result in the formation of by-products and hydrochloric acid that may necessitate the treatment of the combustion gases. This limitation generally leads many engineers to use adsorption-based technologies rather than thermal technologies for the treatment of chlorinated VOCs.

This technology is best suited for soil vapor extraction emission control at heavily contaminated sites. The most frequent application has been in the venting of free-phase hydrocarbons atop the water table. Oftentimes, thermal oxidizers are trailer mounted and are utilized during the initial phase of site remediation when VOC levels are high. As concentrations drop, power/fuel consumption generally rises dramatically, and the trailer-mounted unit is replaced by a more economical treatment method. As a general guideline, a 500-cfm thermal oxidation unit can be purchased for $45,000. Typical fuel consumption for a 500-cfm, 5,000-ppmv VOC airstream is approximately $2,300 per month, based on a natural gas cost of $1.20 per therm (the standard unit of sale for natural gas, representing 100,000 BTU). As the concentration of this vapor stream decreases, the fuel consumption cost required to treat the process stream increases. Using the same example of a 500-cfm flow rate but a reduced concentration of 200 ppmv, the natural gas cost would be approximately $7,300 per month, more than three times the cost of the 500-cfm, 5,000-ppmv VOC airstream.

Catalytic Oxidation

Catalytic oxidation occurs when the contaminant-laden airstream is passed through a catalyst bed that promotes the oxidative destruction of the VOCs to combustion gases. The presence of the catalyst bed allows for the oxidation to occur at a lower temperature than would be required for direct thermal oxidation. The primary advantage of catalytic oxidation is the lower supplemental fuel requirement (BTUs not provided by the VOCs).

The catalyst metal (platinum and/or palladium) surface must be large enough to provide sufficient active areas on which the reactions occur. The catalyst surface must be kept free from dust or other noncombustible materials. Catalysts are subject to both physical and chemical deterioration. Physical deterioration results from mechanical attrition or overheating of the catalyst. Chemical deterioration most frequently is the result of impurities in the VOC stream or from by-product formation. For example, in soil vapor extraction applications of leaded gasoline, catalyst poisoning from the tetra-ethyl and tetra-methyl lead in the gasoline vapors will likely occur. Another form of catalyst deterioration is caused by exposure to halogens or sulfur-containing compounds. Halogen poisoning may occur from entrained water particles that contain chloride (especially in remedial applications involving salt water) or from chlorinated VOCs. Metals in entrained water particles may also act as poisons. Mercury, arsenic, bismuth, antimony, phosphorous, lead, zinc, and other heavy metals are common poisons. Lastly, the presence of high methane levels, (either naturally occurring or escaping from pipelines) may cause catalyst damage. Figure 6-11 shows a photograph of a small electric catalytic oxidizer unit.

Catalytic oxidation burns the VOCs at approximately 600°F for most hydrocarbon remediation applications utilizing a platinum or palladium catalyst. The technology is best suited for treatment of nonhalogenated hydrocarbons to avoid catalyst poisoning. Catalytic oxidizers are generally limited to maximum influent VOC levels in the range of 3,500 ppm (VOCs are a BTU source, and the catalyst has an upper temperature limit). Higher influent concentrations will require

FIGURE 6-11. Small electric catalytic oxidizer. (Photograph provided by Catalytic Combustion Corporation.)

dilution to reduce the influent concentration. Dilution, however, can reduce the extracted volume from the subsurface. A cost analysis is frequently used to justify operation in the catalytic mode using dilution rather than the purchase of a combined catalytic/thermal oxidizer. As a general guideline, a 500-cfm catalytic oxidation unit can be purchased for $50,000 (with heat recovery capabilities) or $40,000 (without heat recovery). Typical fuel consumption for a 500-cfm, 2,000-ppmv VOC airstream is approximately $340 per month (with heat recovery) and $3,200 per month (without heat recovery), based on a natural gas cost of $1.20 per therm. As the concentration of this vapor stream decreases, the fuel consumption cost required to treat the process stream increases. Using the same example of a 500-cfm flow rate and a reduced concentration of 100 ppmv, the natural gas cost would be approximately $1,530 per month (with heat recovery) and $3,200 per month (without heat recovery).

Catalytic oxidizers are available as stand-alone units with auxiliary heat sources or can be purchased as an internal combustion engine as shown in Figure 6-12. The combustion engine unit is attractive for pilot testing applications because it is a self-contained unit with its own fuel source. Internal combustion engine units, however, tend to be less reliable and require more maintenance than conventional units and are limited in capacity.

FIGURE 6-12. Internal combustion engine catalytic oxidizer.

Catalytic oxidizers can also be used to treat chlorinated VOCs but some modifications are necessary and an additional treatment process is required. Because the oxidation of chlorinated compounds creates inorganic acid (hydrochloric acid), the oxidizer needs to be manufactured with acid-resistant materials, and the catalyst needs to be specially manufactured for the acidic conditions. Also, the gas stream exiting the oxidizer needs to be scrubbed to remove the hydrochloric acid vapors. Air scrubbers operate similarly to an air stripper, but instead of stripping chemicals out of the dissolved phase to the vapor phase, chemicals in the vapor phase are dissolved back into the liquid phase. The acid vapors are directed up through a vertical column, and a base solution (typically sodium hydroxide) is sprayed down through the column. The acid in the vapor reacts with the sodium hydroxide solution, and the acid is subsequently removed from the vapor. The sodium hydroxide solution is continuously recirculated through the scrubber, and the acid reacts with the sodium hydroxide to form water and sodium chloride (salt). The recirculating fluid is continuously monitored for pH, and the continuous replacement of the sodium hydroxide coincides with the continuous removal of the salt water. Disposal of the saltwater solution is required.

Although there are manufacturers that produce combined catalytic oxidizers with scrubbing units, the demand is not high enough to manufacture off-the-shelf equipment. These systems are typically custom built for each project. The addition of a scrubber can significantly increase the operation, maintenance, and complexity of the system. The operational costs are difficult to generalize because they are project specific. The incremental cost of scrubber maintenance should be factored into a cost analysis when considering competitive alternatives. A typical capital cost for a 500-cfm catalytic unit with a scrubber for a chlorinated vapor stream is approximately \$150,000 (approximately \$100,000 for the catalytic oxidizer and \$50,000 for the scrubber). The costs for a catalytic oxidizer designed for a chlorinated vapor stream is approximately twice the cost for catalytic oxidizer designed for a nonchlorinated vapor stream. A photograph of a smaller-scale catalytic unit coupled with a scrubber is shown in Figure 6-13.

Biological Technologies

This technology involves the vapor-phase biotreatment of air emissions by biological populations growing on a fixed medium. The fixed medium can be various combinations of plastic support media, compost, manure, wood chips, and other materials. The fixed medium and moisture in the biofilter assist in adsorbing and solubilizing the VOCs for subsequent breakdown by the biological community. Biofilters have been used in the United States since the early 1990s in a limited capacity but have been more widely used in Europe since the 1960s.[3]

Biofilters can provide a low-cost method for treating vapors and can achieve VOC reductions greater than 90 percent but are generally used for lower-concentration vapor streams (<1,500 ppmv), and reductions can be quite variable, between 40 and 90 percent. Biofilters treat vapors that contain biodegradable compounds, which include

FIGURE 6-13. Catalytic oxidizer with integral scrubber. (Photograph provided by Anguil Environmental Systems, Inc.)

short-chain hydrocarbons, monoaromatic hydrocarbons, alcohols, aldehydes, and ketones.[3] The advantage of biofilters is that they provide complete destruction of the VOCs and are not just a collector, such as GAC, that requires further treatment or the disposal of the contaminants. Another significant advantage of biofilters is that they have the ability to treat more water-soluble compounds (acetone, for example).

Two types of biofilters have been used: an enclosed vessel design and open-bed biofilters (engineered soil piles). Both designs operate under the same principles. Within the biofilter, the medium provides an adsorptive material for the VOCs and also acts as a support medium for a biological community. The community can include bacteria, heterotrophs, oligotrophs, and fungi.[3] As with any biological treatment system, the right conditions must be maintained to achieve good removal efficiencies. The parameters important to maintain a healthy biofilter include moisture, temperature, pH, oxygen concentration, and nutrient availability.

There are a number of drawbacks to the biological treatment of vapors. These drawbacks have limited the application of biological treatment and include the following:

- Biological communities require a start-up period to grow and establish the biological community (you can’t just install the system and turn it on).
- Biofilters operate best at steady conditions; it is more typical that vapor concentrations from soil vapor extraction systems are highly variable.
- Moisture conditions can be difficult to maintain, which can significantly affect performance.
- Because of the operational challenges, biofilters can have difficulty consistently meeting regulatory requirements in more regulated areas.
- Back-up vapor treatment systems (usually GAC) may be required to provide the additional treatment necessary to assure regulatory compliance. The cost of these back-up systems may make using the biofilters too expensive.

The optimal situation for biofilters includes a long-term project that yields consistent and low concentration vapors (<500 ppmv) of highly degradable organic compounds and air discharge requirements that are not excessively stringent. This type of application may be a long-term biosparging application or vapor treatment from an air stripper.

Scrubbers for Inorganic Compounds

While most of this chapter has been devoted to organic compounds, some soil vapor extraction remediation sites may have inorganic compounds in the contaminated airstream. Hydrogen sulfide is probably the most widely found inorganic contaminant at impacted sites. Some sites have been known to have up to 30,000 ppmv of hydrogen sulfide in the extracted airstream.

Chemical scrubbers can be used to remove the hydrogen sulfide from the airstream. As previously discussed, the scrubber looks very similar to an air stripper but operates in reverse. The air/water contact serves to remove the contaminants from the air and transfer them to the water stream. The water can then be treated with caustic and an oxidizing agent (hydrogen peroxide, ozone, supersaturated oxygen) to destroy the hydrogen sulfide. The high pH increases the rate of hydrogen sulfide transfer, and the oxidizing agent hydrolyzes the hydrogen sulfide. This rapid reaction tends to maximize the driving gradient from the air to the water. In some instances (low concentrations: 50-ppmv range), the hydrogen sulfide in air may be treated biologically rather than oxidatively. Scrubbers can also be used to treat ammonia gases that may be generated in water-treatment operations. The scrubber operates similarly to the hydrogen sulfide systems discussed above. The recirculation fluids through the scrubber are typically nitric acid and sulfuric acid. The ammonia gas will react with the nitric acid to form ammonia nitrate, and the sulfuric acid will react to form ammonium sulfate. These resulting liquid products can be used as fertilizers.

Technology Selection Summary

Vapor emissions from site remediation should be evaluated on a case-by-case basis, based on the available site characterization data, regulatory requirements, life cycle considerations, and other project-specific data as previously outlined. Some generalizations, however, can be formulated regarding technology selection. Thermal oxidation is generally best suited for high hydrocarbon VOC situations, such as soil vapor extraction emissions at sites impacted by NAPL. Catalytic oxidation is best utilized at hydrocarbon sites with moderate VOC impacts and low to moderate airflows. This can be found at a typical service station site without NAPL but high to moderate soil contamination. Catalytic oxidation of chlorinated hydrocarbons is best utilized at sites with moderate VOC impacts and moderate airflows. Off-site regenerable GAC is best utilized in instances in which the mass loading

TABLE 6-5 Air Treatment Technology Selection Guidelines

Technology	Most Applicable VOCs	Most Applicable Airflow	Most Applicable Mass Loadings
GAC—off-site regeneration	HC, CVOCs	All	Low
GAC—on-site regeneration	HC, CVOCs	All	Moderate
Regenerable resin	CVOCs	All	Moderate
Catalytic oxidation	HC	Low to moderate	Moderate
Thermal oxidation	HC	Low to moderate	High
Biofilters	Soluble HC	Low to moderate	Low to moderate

Note. Reader is advised to use this table as a general guideline only. HC, hydrocarbons; CVOCs, chlorinated volatile organic compounds.

Airflow
  Low = 100 scfm
  Moderate = 500 scfm
  High = >2,000 scfm
Mass loading
  Low = 5 pounds per day range
  Moderate = 50 pounds per day range
  High = 100 pounds per day

is low. Steam-regenerable GAC is best applied at high airflows (no need to heat the air) and moderate VOC concentrations (low regeneration frequency). Steam-regenerable GAC is applicable for most VOCs, but its isotherms should be checked for the individual compound to ensure that regeneration frequency is acceptable. A resin adsorption system is best utilized for halogenated VOC airstreams with moderate contamination. Biofilters are best suited for the treatment of low to moderate concentrations of soluble and biodegradable VOCs such as BTEX and ketones at low to moderate airflows. Biofilters tend to be bulky; therefore, large mass loadings require very large units. Table 6-5 provides these general guidelines in a tabular format. Life cycle concentrations may require a combination of these technologies for the most cost-effective air emission control design.

EMISSION CONTROL CASE STUDY

Thus far, we have introduced the design considerations for chemical, physical, and biological processes typically used for emission controls at remediation sites. General guidelines for when and where to install these systems have also been provided. Following is an actual case study that demonstrates the application of these concepts from a discussion of site characteristics, alternatives, and actual performance data. In particular, these performance data highlight the life cycle design concept using both predicted and actual system operation. Please note that the following case study was completed during the late 1990s so the costs provided do not represent present-day costs.

Site Description

The site is a former solvent and chemical waste recycling facility located on approximately 8 acres in Michigan. Facility operations, which included the storage, handling, and processing of waste solvents and other chemicals, resulted in the release of contaminants into the environment. In the early 1980s, operations were discontinued, initial site investigations were conducted, and the site was added to the National Priorities List in 1986.

During the investigation, the site was subdivided into three distinct units, which are depicted in Figure 6-14 as follows:

- Zone A — solvent loading area
- Zone B — solvent processing area
- Zone C — soil berm area

The primary contaminants of concern were consistent between the three zones and included VOCs, in particular, tetrachloroethene, trichloroethene, and *cis*-1,2 dichloroethene (a biological breakdown product of both tetrachloroethene and trichloroethene). Trace concentrations of other VOCs and semi-volatile organic compounds (SVOCs) were also found during the remedial investigation. These compounds, however, did not play a significant role in the selection of the vapor control system for the site.

In zone A, an LNAPL was also discovered in an approximately 31,000-square-foot (3/4-acre) area with a maximum apparent thickness of nearly 5 feet. Through analysis, this

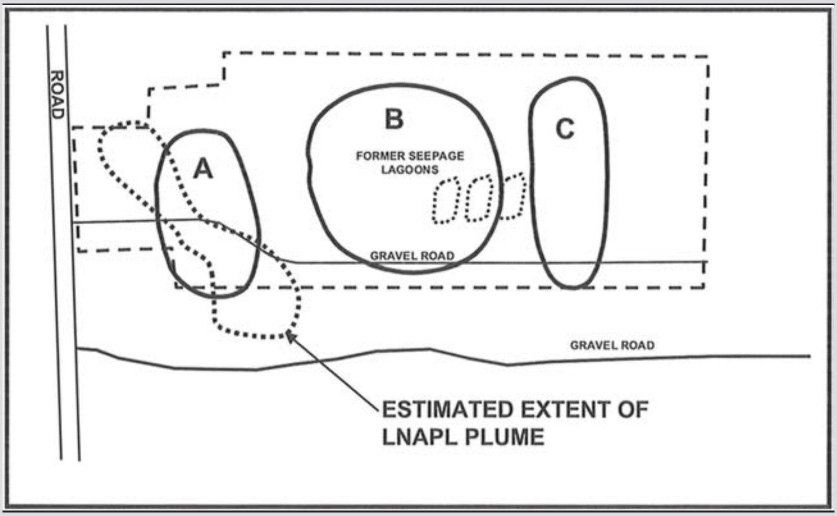


FIGURE 6-14. Case study layout.

LNAPL was found to be primarily mineral spirits (a hydrocarbon-based solvent) that also contained appreciable concentrations of dissolved chlorinated VOCs.

Soils at the site are typically fine-grained sands extending from the ground surface to approximately 40 feet below grade. A confining bed of silty clay was found beneath this surficial sand, effectively limiting the downward migration of contaminants released at the site. Within the surficial sand, a thin (5- to 20-foot-thick) water-table aquifer is present. Dissolved contaminants were found within that aquifer.

Remedial Approach

The remedial strategy adopted for this site combined several technologies to address the different phases of contamination. A selective, product-only skimming system was installed in zone A to remove the mobile fraction of the LNAPL plume. Soil vapor extraction was also chosen to remove the residual, immobile non-aqueous-phase liquid (NAPL) within that zone. Soil vapor extraction was also selected to address the soil impacts found in each of the three zones at the site. An air-sparging system was installed in each of the zones to address the dissolved and residual contaminants below the water table.

The active phase of the remedial program continued until contaminant mass recovery rates reached asymptotic levels. When conditions reached levels protective of human health and the environment (consistent with the requirements of the Record of Decision), natural attenuation processes were relied on to achieve final site closure. Until natural attenuation could be applied, vapor withdrawal and treatment were needed.

Emission Control Design Basis

Pilot tests were conducted at the site to define the radii of influence for both the soil vapor extraction and air-sparging systems. Given the size and complexity of the site, vapor flow modeling was used to optimize the number, placement, and operating conditions (applied vacuum and flow) for the soil vapor extraction system. From the pilot testing and modeling results, the radial influence of the soil vapor extraction and air-sparging wells were approximately 50 and 20 feet, respectively. A summary of the final design is as follows:

Zone A	
Soil vapor extraction wells	17 wells @ 35 cfm/well (595 cfm total extracted flow)
Air-sparging wells	20 wells @ 8 cfm/well (160 cfm total injected flow)
Zone B	
Soil vapor extraction wells	20 wells @ 35 cfm/well (700 cfm total extracted flow)
Air-sparging wells	27 wells @ 8 cfm/well (216 cfm total injected flow)
Zone C	
Soil vapor extraction wells	10 wells @ 28 cfm/well (280 cfm total extracted flow)
Air-sparging wells	10 wells @ 8 cfm/well (80 cfm total injected flow)

When operating together, the soil vapor extraction system for all three zones required a soil vapor extraction and treatment capacity of nearly 1,600 cfm. Soil vapor samples collected during the pilot tests were used to estimate the concentration of vapor-phase contaminants reaching the future emission control system. From those samples, a maximum VOC recovery rate of over 40 pounds per day was determined as the design criteria for the off-gas control system.

Emission limits were determined based on the requirements of the local oversight agency (in this case the Michigan Department of Environmental Quality). Dispersion modeling was used to evaluate the impact of emissions from the soil vapor extraction system on the surrounding area.

Alternatives Evaluation

Given the presence of LNAPL in zone A and experience at many other sites, the concentration of vapor-phase contaminants from the soil vapor extraction system were expected to remain elevated for an extended duration. While GAC alone was selected for use in zones B and C, the GAC in zone A was expected to be rapidly and frequently exhausted so several emission control alternatives were evaluated for use in that zone. After an initial screening, a detailed evaluation was conducted of the following emission control alternatives:

- Carbon (off-site regeneration)
- Carbon (on-site regeneration)
- Catalytic oxidation
- Catalytic oxidation with scrubber
- Thermal oxidation
- Thermal oxidation with scrubber

Each of the above systems was capable of collecting (carbon systems) or destroying (oxidation systems) the recovered vapor-phase contaminants in compliance with emission limits. The final system selection, therefore, was based on a cost–benefit analysis performed during the preliminary design phase of the project. This analysis was specifically based on the life cycle design approach.

Off-site regenerable GAC would ultimately be used in the later stages of the project when vapor concentrations declined to low levels. But based on experience and as summarized previously, oxidation technologies are inappropriate for the high-flow, low-concentration vapor streams as would ultimately be the conditions at this site. The evaluation of alternative technologies was based on incremental costs with GAC as a baseline. On that basis, no capital costs were assigned to an off-site regenerable GAC system.

Table 6-6 provides a summary of the cost analysis conducted for the zone A treatment system. The cost analysis was conducted for a range of project durations, extending to two years (the maximum project duration anticipated for this area of the site). As shown in the table, catalytic oxidation

TABLE 6-6 Case Study — Off-gas Cost Analysis Summary

Technology	Capital Cost[a] ($)	O&M Estimated per Week[b] ($)	Cumulative Cost after 26 weeks ($)	Cumulative Cost after 52 weeks ($)	Cumulative Cost after 156 weeks ($)
GAC — off-site regeneration[c]	0	2,521	65,546	131,092	393,276
GAC — on-site regeneration	220,000	360	229,360	238,720	276,160
Catalytic oxidation	115,000	164	119,264	123,528	140,584
Catalytic oxidation w/scrubber	200,000	216	205,616	211,232	233,696
Thermal oxidation	62,000	605	77,730	93,460	156,380
Thermal oxidation w/scrubber	137,000	660	154,160	171,320	239,960

Note. Costs presented in this table were developed in the late 1990s and are not reflective of current costs.

[a] Capital costs include equipment only.

[b] O&M estimated costs provided by vendor in response to in situ vapor extraction pilot test results.

[c] Assumes using proposed vapor-phase carbon system for zones A, B, and C of phase III soil vapor extraction systems.

was projected to have the lowest overall cost (including both capital and operational expenses) at the end of a two-year period. The estimated margin between thermal and catalytic systems, however, was not significant ($125,000 for thermal and $132,000 for catalytic oxidation). Considering the lower operating temperature (less system fatigue) and fewer objectionable combustion by-products, catalytic oxidation was selected for implementation.

As described previously in this chapter, both thermal and catalytic oxidation technologies, when applied with chlorinated VOCs, will result in the formation of hydrochloric acid in the exhaust stream. On that basis, oxidation systems combined with acid-gas scrubbers were included in the list of considered emission control systems. Based on the long-term projections for influent VOC concentrations (again the life cycle approach), combined with dispersion modeling conducted for the permit application, the exhaust stream for this site did not require a scrubber system.

System Performance

Although the emission control alternatives evaluation and selection of catalytic oxidation was conducted specifically for zone A, the implemented design allowed the use of the oxidizer at any of the three zones. This added system flexibility allowed for the application of the most cost-effective emission control scheme at any time during the project.

Since all three zones would have a life cycle reduction in concentration over the life of the system, it was decided to optimize the use of the catalytic oxidizer. The carbon system was designed to be able to treat the entire 1,800-cfm stream from the combined three zones. The catalytic oxidizer was designed to treat the flow from only one zone at a time. Initially, only one zone was turned on. Its high-concentration stream was sent to the catalytic oxidizer. When the concentration in that stream was below the cost-effective use of the oxidizer, the airstream was rerouted to the carbon system. A new zone was started up, and that high-concentration waste stream was now sent to the catalytic oxidizer. This life cycle design maximized the use of the catalytic oxidizer while still

TABLE 6-7 Case Study — Summary of Daily Operating Costs

Date	Estimated Catalytic Oxidizer Operating Costs (dollars per day)	Theoretical GAC Consumption Rate (dollars per day)
15 Aug 98	61	183
20 Aug 98	65	138
29 Aug 98	52	110
5 Sep 98	52	98
11 Sep 98	62	106
19 Sep 98	60	100
26 Sep 98	60	98
1 Oct 98	78	120
21 Oct 98	105	342
27 Oct 98	91	236
21 Nov 98	73	134
19 Dec 98	86	202
22 Jan 99	56	93
26 Feb 99	107	108
4 Apr 99	87	298
29 Apr 99	84	93
11 Jun 99	112	88
17 Jul 99	101	46
22 Aug 99	103	80

using the more cost-effective carbon for low-concentration streams.

Table 6-7 provides a summary of daily costs for the operation of the catalytic oxidizer. To monitor the relative cost of competing emission control systems, Table 6-7 also includes calculated carbon consumption estimates using influent analytical data collected during system operation. Figure 6-15 provides a graphical presentation of these data throughout the first year's operation.

As shown in Figure 6-15, the daily cost of operation for the catalytic oxidizer was generally consistent, within a narrow range from approximately \$50 to \$100 per day. As expected, operational costs for an oxidizer are not directly dependent on the influent vapor composition within the range of concentrations processed by this system. Supplemental gas consumption, the primary system operation expense, is more a function of system flow rate and set point temperature than the VOC loading.

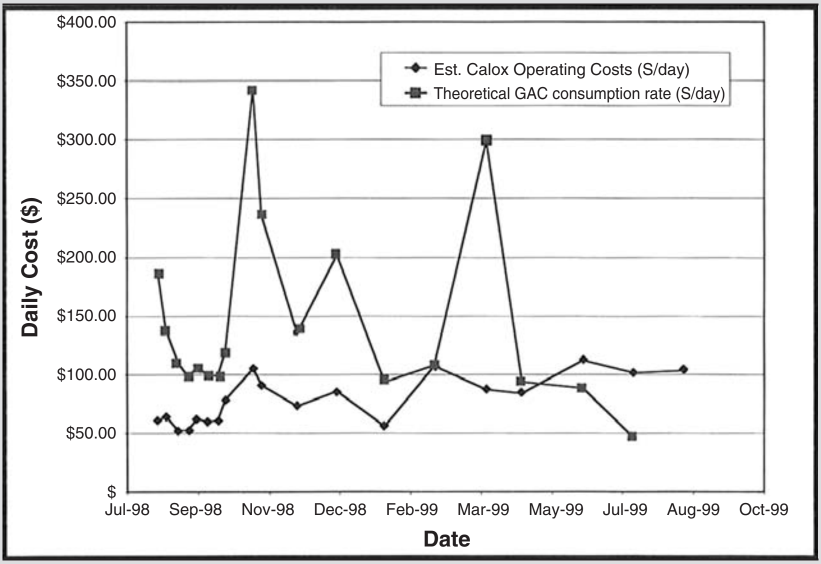


FIGURE 6-15. Case study — summary of daily operating cost.

In contrast to the oxidizer daily costs, carbon costs are directly related to the VOC loading. For this reason, the estimated (calculated) costs for carbon treatment varied widely during the first year of operation. Except for concentration spikes that followed a period of extended downtime and the startup of the air-sparging system, influent vapor concentrations generally declined with time (Figure 6-16). As shown in Figure 6-15, the daily cost for carbon treatment reached levels that were consistently below the daily cost for operating the oxidizer. The crossover point is depicted in Figure 6-16 at approximately May 1999. With this finding, the operation of the oxidizer for zone B was discontinued, and that vapor flow stream was sent to the on-site GAC system. Zone A was then started up, and its vapor flow stream was routed through the oxidizer to treat the initial, high-concentration vapor stream. Daily costs were again monitored for that area to determine when carbon would be more appropriate and cost effective for continued operation. When zone A had completed its catalytic

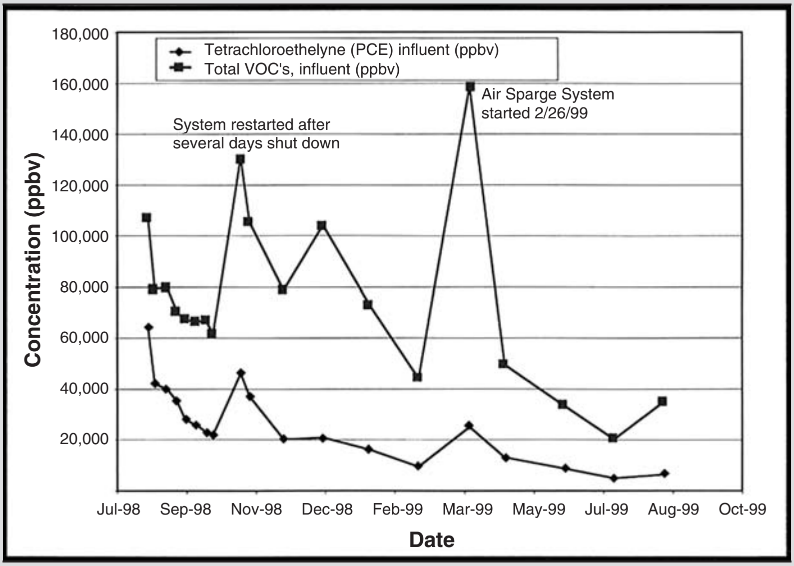


FIGURE 6-16. Case study — influent vapor composition.

operations, then zone C would be turned on and would go through the same process.

By breaking the treatment system into three zones, this design was able to maximize the use of the most cost-effective treatment technology. Normally, a designer has to decide between the technology that works best at high concentrations, paying for increased operation costs as concentrations decrease, and the technology that works best at low concentrations, paying for increased operation costs at the beginning of treatment. This design avoided both of those problems. The only problem with this design solution was that the total time of operation for the entire system was extended because of the phased approach. However, the economic analysis for this site indicated that this approach was still the most cost effective. Although this approach worked for this site, the various cost factors associated with other sites for which this approach is considered need to be evaluated to determine if it is best solution for their respective conditions.

References

1. Noll, K.E., Vassilios, G., and Hou, W.S., Adsorption Technology for Air and Water Pollution Control, Lewis, 1992.
2. Faust, S.D., and O.M., Aly, Adsorption Processes for Water Treatment, Butterworth, 1987.
3. United States Environmental Protection Agency, Off-gas Treatment Technologies for Soil Vapor Extraction Systems: State of the Practice, Office of Superfund Remediation and Technology Innovation, EPA-542-R-05-028, March 2006.
4. Bethea, R.M., Air Pollution Control Technology, Van Nostrand Reinhold, 1978.

7

Operations of Treatment Systems

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A comprehensive operation and maintenance program is a critical component of any successful groundwater treatment system. Even the best-designed system requires a well thought-out and implemented program to ensure effective and continuous operation. Both operation and maintenance, although definitively connected, serve unique and equally important roles in any treatment program. In this chapter, we discuss the basic principles of each, including information on specific challenges associated with groundwater treatment systems. In addition, we provide information regarding record keeping, system evaluation and optimization, and health and safety concerns related to treatment systems.

PRINCIPLES OF OPERATION

The basic idea of operating a system is self-explanatory. However, operating a treatment system can be very complex, especially when dealing with the unique challenges of groundwater treatment. The process of operations begins during the design phase when engineers are considering the most appropriate equipment for a specific operation, compatibility of materials, degree of operational flexibility required, and the degree of manual versus automated control. These concepts are carried into the actual operation of the system as the system is monitored to assure that it is operating as intended. The following sections discuss the basic principles and challenges of system operation.

Elements Unique to Groundwater Remediation

Although many of the technologies discussed in this book are considered to be mature when applied within the fairly predictable flows

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associated with the municipal or industrial treatment sector, when they are applied to the treatment of contaminated groundwater, unique challenges can arise. Not only must we design for the removal of the contaminants within the groundwater but we also have to account for the elements unique to groundwater treatment, particularly the variations in contaminant concentrations over time, potential inorganic loading from silt/sand mined from the aquifer by the extraction wells, and potentially high concentrations of dissolved metals within extracted groundwater.

Variations in Concentration

In Chapter 1, we discussed the time effect on concentration. Removal of the contaminants by the treatment system combined with the dilution effect by clean water entering the affected site produces a steady decline in contaminant concentrations in the groundwater (Figure 7-1). Although true in some instances, it cannot be assumed that the lower the influent concentration, the better (or more efficiently) the treatment system will operate. Certain unit processes are designed based on a minimum concentration and may lose efficiency as the concentrations decrease, or may not function at all after a minimum concentration threshold is reached. In either case, the design must be able to accommodate the entire life cycle concentration of the project.

One example of the time effect on concentrations is in the use of biological treatment systems for groundwater treatment. A continuous source of contaminants is necessary to sustain the microorganisms

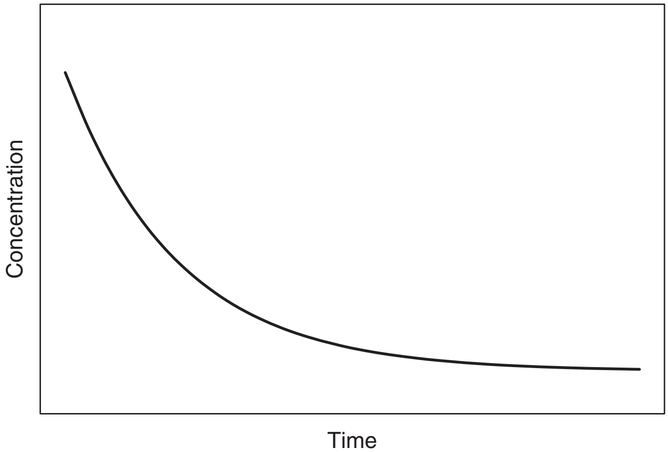


FIGURE 7-1. Time effect on concentration in an extraction well.

within the biological reactor. As the concentration of contaminants decreases, the viability of the microbial community within the reactor decreases as well. To overcome this decrease in concentration, the operator may have to increase the rate of sludge return to the reactor or increase the hydraulic residence time to ensure sufficient treatment. However, if the concentrations decrease too much, the microbial community may be unsustainable and may require a supplemental source of carbon (provided that this option is cost effective).

A second example of the time effect on concentration is the use of liquid-phase GAC. Decreases in groundwater concentrations over time will correspond to an overall decrease in the loading to each carbon bed (assuming that the groundwater pumping rate remains constant). This decrease in contaminant loading will correspond to an increase in the period of time between each change out, which in turn will lead to an overall cost savings for the project. Chapter 1 provides a more complete explanation of both of these examples.

Sand and Silt Production

Sand and silt production from the aquifer is one of the most significant challenges in designing a groundwater extraction well. Unlike potable water extraction, in which the most permeable and best-producing aquifer zones are selectively targeted, the extraction of contaminated groundwater must be completed in the zone in which the contamination is present, regardless of the aquifer's permeability or ability to produce water. It is not uncommon for contaminants to exist in low-permeability aquifer zones that are marginal water producers. With that said, the design and installation of the extraction system as a whole (a sufficient number of extraction points to limit the overextraction on an individual well), as well as the individual extraction wells (screen type, slot size, filter pack, etc.), are critical to limiting the production of sand and silt, while maximizing the quantity and quality of water extracted.

It is important to keep in mind that, in the world of groundwater remediation, all wells are not created equal. The design, installation, and development of wells for groundwater extraction are very different than for groundwater monitoring. In the name of efficiency and to reduce costs, the industry has adopted standardized monitoring well installation designs. However, these designs often minimize screen slot sizes and filter packs to minimize turbidity, typically at the expense of water production. Although this may be acceptable for monitoring wells, where only several liters of water need to be pumped during a sampling event, the well screen and filter pack for extraction well production must be matched to the aquifer materials to maximize well efficiency.

As an example, the authors are aware of a site at which an extraction well was screened in a silt/fine sand material. When the well was installed, a larger slot size was selected to facilitate higher flow rates from the well without consideration for the grain size of the aquifer material. The larger slot size allowed for the aquifer materials to readily pass through the screen, and over time, the pumping resulted in the mining out of a large quantity of aquifer material. Eventually, the removal of the silt and sand created a large enough void that it collapsed, damaging the well and generating a sink hole several feet in depth (Figure 7-2).

In addition, within the same system, the silt and sand material led to siltation in the conveyance piping, the fouling of the system, and an increase in the quantity of sludge generated from the system. If conditions allow for gravity settling or the filtering out of the materials, then silt and sand material can collect at any location in the system, such as equalization tanks, air-stripper sumps, GAC tanks, oil/water separators, and even in pipes if the groundwater velocity is not sufficient to scour (Figure 7-3).

The method of well installation can significantly affect well efficiency. For example, environmental professionals have been using techniques to maximize drilling speed and lithologic screening, such as rotosonic drilling. Well installations utilizing these methods can lead to boreholes that are smeared or formations that are compacted as a result of vibration. These issues can have a detrimental effect on well

FIGURE 7-2. Sinkhole created by the mining of the formation by the extraction well.

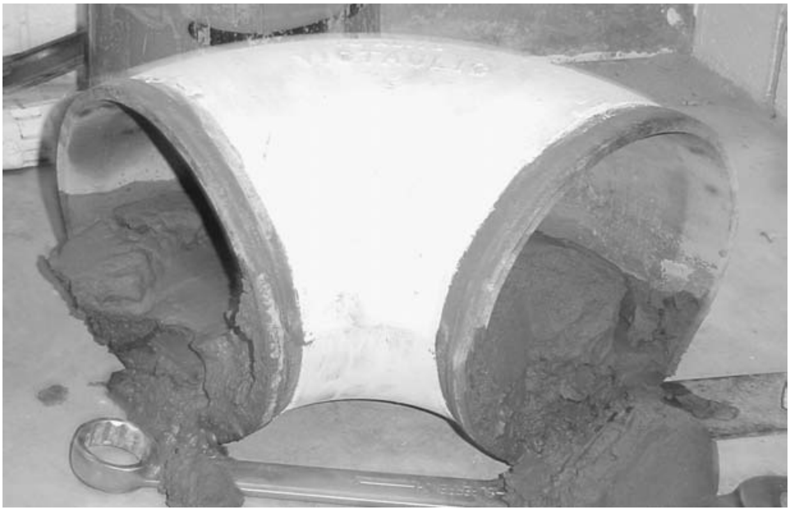


FIGURE 7-3. Silt material collected in the system piping.

efficiency and water production, and aggressive well development may be necessary to overcome these problems.

After the proper well screen and filter pack have been selected and installed, the well must be properly developed to ensure effective water production. This is not a one- or two-hour effort as is the case for most monitoring well installations. Proper extraction well development can take several days to a week, depending on the formation and installation method.

Even with proper design, installation, and development of extraction wells, some sand and silt will still get into most systems. It is important to keep this in mind when considering the operation and maintenance of systems. Not only will silt and sand collect within the system, but their accumulation can lead to pump seal failure, the pitting/erosion of pump impellers, and damage to valves and piping. Filtering systems such as bag filters or cartridge filters can be used to minimize the quantity of aquifer materials that enter the treatment system, but even with in-line filtering, some material will get through. Equipment should be checked routinely for wear and replaced as necessary.

Dissolved Metals

The presence of contaminants within the aquifer can alter the geochemistry of the groundwater and make the extracted groundwater more difficult to treat. For example, the presence of biodegradable organic contaminants can create reducing conditions that in turn can lead to high dissolved metals concentrations. These high concentrations are caused by the dissolution of metals from the aquifer soils under reducing conditions. Numerous metals can be bound up within the aquifer materials, each of which can be released under these conditions. Iron and manganese are the most commonly observed because of their relatively high abundance in soils. In addition, the reducing conditions in the subsurface often cause an increase in the natural hardness of the groundwater (caused by dissolved calcium and magnesium).

These dissolved metals can precipitate on well screens, in pipes, or on treatment system components and lead to operational and maintenance issues as a result of this scaling. Often the precipitation of these metals is brought about by processes within the system. One of the more common operations that cause metals precipitation is the aeration of groundwater. The introduction of air into the groundwater can oxidize the iron and manganese; oxidized iron and manganese have a low solubility, thus forming precipitates within the system. Another problem common to aeration is the deposition of scale as a result of the stripping of carbon dioxide from the water. As the carbon dioxide is removed, the pH increases, and the resulting conditions cause a shift in the carbonate equilibrium and the deposition of calcium carbonate within the system. A more thorough discussion of metals precipitation during aeration can be found in Chapter 2.

We recently observed two separate metals precipitation problems in an aboveground groundwater treatment system. The system was designed to biologically treat a groundwater containing a high concentration of organics (average influent BOD of 1,000 mg/L). The treatment train consisted of a two-stage, submerged fixed-film bioreactor that was pretreating the groundwater prior to discharge to the local sewage treatment plant. With the high amount of organics in the subsurface groundwater system, reducing conditions were prevalent and contributed to a high dissolved metals concentration in the extracted groundwater, particularly iron and magnesium. During treatment, we typically see these dissolved metals precipitate with some attachment to the submerged media and the biogrowth; however, the force of mixing (in this case, coarse bubble aeration diffusers) is usually sufficient to shear the solids as they build up. The sheared solids are subsequently carried over to a clarifier where they are removed from the process stream. In this instance however, the high dissolved metals concentrations (and associated precipitation), combined with rapid biological growth as a result of high organic loading rates, overwhelmed the shear available in the system, resulting in the complete

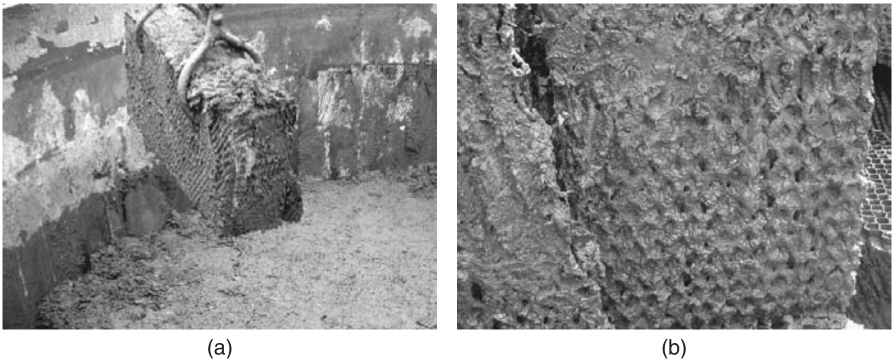


FIGURE 7-4. Plugged fixed-film bioreactor medium.

plugging of the submerged media. Photos of the media during system cleaning are shown in Figure 7-4.

Ultimately, this metals precipitation problem was solved by converting the first stage of the system to a suspended growth reactor and utilizing an intermediate clarifier ahead of the second-stage fixed-film bioreactor, thus allowing the intermediate clarifier to remove a majority of the precipitated metals prior to reaching the fixed-film unit. Solids from the intermediate clarifier were also returned to the first-stage suspended growth reactor to control sludge age and the MLSS concentration in that reactor.

The second metals precipitation problem that occurred with this system was related to the nutrient feed system. Nutrients in the form of a urea–ammonium–phosphate mixture were being injected into a 2-inch bioreactor recirculation loop; however, a high magnesium concentration in the groundwater, combined with turbulence from the recirculation pump and the addition of the nutrients, resulted in the formation of struvite. The resulting precipitate caused mechanical problems with the recirculation pumps, requiring excessive maintenance. The solution in this case was to relocate the nutrient injection into the influent header pipe and eliminate the high concentration of ammonia and phosphate within the recirculation loop.

Finally, it is important to note that although the precipitation of metals within the system may be brought about by a specific treatment process, the effects of the precipitation may not be confined to that process. Deposition of the precipitated metals may continue downstream of the process, particularly within piping and valves, creating issues throughout the system.

Treatment System Reliability

Another area in which groundwater remediation design is unique is in the life expectancy of the project. When we deal with wastewater treatment systems, we normally design for a 20- to 30-year life. This number represents the life expectancy of the equipment not the life expectancy of the project. With only a few exceptions (i.e., leachate treatment) groundwater treatment systems will operate over much shorter periods of time, and the controlling parameter is usually the life expectancy of the project. Two key considerations in system reliability are a focus on equipment reliability during design and operation, and consideration of the types of materials specified during the design of the system.

Equipment Reliability

During the treatment system design, as well as during operation, the design engineer needs to focus on equipment reliability and operational uptime. The design engineer must take into consideration potential process and/or equipment interactions that might result in reduced equipment performance, unnecessary operator intervention, or premature equipment failure.

Probably the single most important reliability issue for any treatment system is rotating equipment. Pumps, blowers, compressors, and other rotating equipment are all critical components of any treatment system, and it is impossible to design a system that does not utilize them to transfer fluids or air within the system. The failure of rotating components in systems is not uncommon and can be brought on by numerous conditions, such as poor lubrication of equipment, pumping of abrasive or corrosive materials, or operation outside of its specifications.

As an example of a failure of a rotating part, the authors are aware of a site that utilizes several pumps for the transfer of return and waste-activated sludge. This sludge contains a high percentage of metals as a result of the high iron and magnesium loading from the groundwater plume. The precipitated metals solids in the sludge are very abrasive and during pilot testing caused the mechanical seals on the sludge pumps to fail as a result of wear, which in turn caused the sludge to leak from the pump. Therefore during the design of the full-scale system, a double mechanical seal with a pressurized seal flush was specified for the sludge pumps. A double mechanical seal is designed with a primary seal (similar to a single mechanical seal) and a secondary seal, and the space between the two seals is pressurized with a fluid, in this case potable water. As with single mechanical seals, double mechanical seals will ultimately fail, but they are designed to last considerably longer and are ideal for use with abrasive fluids and corrosive fluids or other process fluids that could create a hazard if they leaked.

The key to equipment reliability throughout the period of system operation is routine maintenance and inspections of the process equipment by the system operators. The equipment should be maintained according to the manufacturer's specifications at all times. If the operator detects changes in the way the equipment is performing, such as changes in operation, noise, or vibration, the suspect piece of equipment needs to be evaluated to determine the cause of the condition before catastrophic failure occurs. There will always be the potential for the failure of equipment, but through good design practices and attentive maintenance, the potential for failure can be reduced significantly.

The most prevalent cause of failure of groundwater treatment systems is the lack of maintenance. Either the project does not put together an operation and maintenance manual and the related maintenance schedule, or the owner of the site does not put into the budget time and materials for regular maintenance. The pumps and blowers do not get oil, the valves do not get checked, and the pipes are allowed to scale. Only when an actual failure occurs does someone check the equipment. Even if you expect the system to run for only one to two years, maintenance should be part of your program.

Materials of Construction

The materials used to convey process fluids throughout the treatment system will play an important role in system reliability. The most obvious determination that needs to be made is whether the process fluid is compatible with the materials of construction for the process equipment it comes into contact with, as well as the process lines that the fluid runs through. There are a number of resources available that will present corrosion and general compatibility information. These should be consulted to determine the appropriate materials of construction for the process stream. All wetted parts should be checked for compatibility, including pump seals, valve seals, and instrumentation, which are often overlooked.

When specifying materials, consideration must also be given to process flows that are a combination of two or more process streams. It is easy to determine the most appropriate material for single fluids. However, it may be that the combined process flow stream might have different physical properties than the individual process fluids. Probably the best example of this is adding an acid or a base and the resulting heat generated from the reaction.

Finally, maintaining coatings and paint on tanks and equipment is an important maintenance task that should not be overlooked. The operating conditions of treatment systems can be very hard on these coated surfaces (such as at the air/water interface in aerobic tanks) and may require periodic maintenance to ensure that the corrosion of metal does not compromise the integrity of the equipment

Treatment System Flexibility

Maintaining operational flexibility is a key component of the design engineer's job when determining the process flow and equipment that needs to be included in the design. Without adequate flexibility, unnecessary amounts of downtime, both equipment and process, may be realized. Flexibility should be incorporated both from the perspective of limiting downtime, as well as accounting for variations in both contaminant and hydraulic loading over time.

Multiple Treatment Units

The easiest way to maintain operational flexibility is to include multiple treatment units in the design. For example, if a single transfer pump is incorporated into the design at a location that is critical to the operation of the system as a whole, it would be beneficial to supply an appropriately plumbed second pump that could be brought on-line relatively quickly when and if the first pump failed. A recent design utilized a pump that was designed for mixing polymer in a solids tank prior to the solids being fed to a filter press but also was capable of being used as a spare for a secondary process. Although the pump will operate only for short periods of time during the dewatering operations, it will greatly improve the operational flexibility of the system as a whole.

On a larger scale, designs can incorporate multiple treatment trains. A design performed in the Midwest incorporated two treatment trains to the point of sludge dewatering operations. This included two activated sludge reactors (1st stage), two submerged fixed-film biological reactors (2nd stage), and two clarifiers following each of the 1st- and 2nd-stage biological treatment operations (a total of four clarifiers). Great operational flexibility was realized using this design. For example, during start-up operations, a single treatment train was used because contaminant and hydraulic loading rates to the system were not sufficient to warrant the operation of both treatment trains. Full system operations are designed to utilize both treatment trains. Over time, the contaminant and hydraulic loading rates to the system are expected to decrease, ultimately requiring the operation of only one treatment train at a time. This will save considerable labor and operational costs, especially in the cost of electricity for the aeration system.

Another advantage to incorporating a second piece of equipment is for process control requirements. Let's assume controlling the level within a storage tank is critical to a system's operations. If two pumps are appropriately plumbed and valved, the second pump can be initiated, by system interlock, if the liquid level within the storage tank rises above a predetermined high set point (this is known as a lead/lag pumping configuration). The second pump can then be disabled when the liquid level reaches another, lower predetermined set point. This allows for two smaller pumps to be installed, which when combined are capable of handling periodic high flow rates. The second pump can serve as a spare for handing at least a portion of the total flow if the first pump fails, and operating one smaller pump will reduce energy costs.

Portable and Rented Equipment

Using portable equipment may increase the operational flexibility and cost effectiveness of the project, especially if the equipment is not necessary for day-to-day operations or will not be required on a continuous basis. It will be in the hands of the design engineer to perform appropriate cost analyses to determine the most cost-effective solution for the project.

A good example of the use of mobile equipment is a trailer-mounted soil-vapor extraction system (Figure 7-5). The authors have used portable soil vapor extraction trailers with great efficiency at a site where biological activity results in the accumulation of methane in the subsurface. Subsurface pressures are measured using soil-gas probes within a contaminated plume area. If too much pressure is being generated, a soil-vapor extraction unit is transported to the area and operated until the subsurface pressure is negated. The use of a mobile soil-vapor extraction unit saves significant capital cost and operator attention when compared to the installation and maintenance of multiple permanent soil-vapor extraction systems.

There is also a wide range of equipment that can be rented on a temporary basis for use at a site, including bulk storage tanks (i.e., frac tanks), power generation equipment, compressors, GAC carbon tanks, pumps, and even whole skid- or trailer-mounted treatment units such

FIGURE 7-5. Trailer-mounted mobile soil vapor-extraction unit.

as the soil-vapor extraction units mentioned above. The flexibility provided by the short-term rental of portable equipment rather than purchasing equipment is obvious. However, the costs of renting over long periods can sometimes add up to several times the purchase price of the equipment. The costs of purchasing and maintaining the equipment over the duration of use should be compared with the total cost of the rental equipment to determine what is best for each specific situation.

Operator Attention and Expense

As discussed in Chapter 1, the cost of an operator can be a significant percentage of the overall operating costs of the life cycle of a system, and the design engineer should make every effort to minimize the amount of operator attention needed for the system. This can be done at every stage of the design from the selection of the treatment technology to the selection of equipment. For example, some treatment technologies, such as biological systems, require more intensive operator attention than a GAC system that can operate largely unattended for longer periods. Another way of reducing the operator expense is by automating the monitoring and control of the system, which is discussed in more detail in the following section. Finally, equipment requiring limited maintenance should be chosen, if possible. A good example of this would be the selection of a regenerative blower that requires minimal routine maintenance rather than a belt-driven rotary lobe blower that requires routine greasing (as often as once per week), oil changes, and belt replacement.

Another important aspect of cost savings both in terms of operator time and system operating cost is utilizing properly trained and qualified operators to maintain the systems. Operators who are properly trained in the operation of the specific equipment within the system will help to ensure that the equipment is being properly maintained and that problems within the system are more readily diagnosed. Operating a remediation system is often learned in the field by working under the supervision of more experienced personnel. This type of hands-on training is an effective way to expose operating personnel to the wide variety of remediation systems typically in use. To the extent possible, personnel who will be responsible for the operation of the system should be involved in the design, construction, and equipment testing phases.

One final note on treatment system operators is that some agencies may require the treatment system operator to be licensed to operate certain treatment technologies or to be licensed to operate a system that discharges treated water under certain discharge permits. Often this licensing requires additional training or a specified number of years of experience. These requirements may make finding a qualified operator more difficult. The design engineer should be knowledgeable of the local regulatory requirements prior to system design to evaluate the need for licensed operators.

Automation of Control and Monitoring

The level of automation of a treatment system can vary significantly from simple systems such as one that may control a single pump to drain a tank, through a sophisticated, fully automated system that may operate dozens of pieces of equipment and monitoring instruments. The automation of a system is accomplished by using supervisory control and data acquisition (SCADA) systems. SCADA systems are used to monitor and control both individual pieces of equipment and treatment processes, all from a single centralized location.

Components of Supervisory Control and Data Acquisition System

The SCADA system can be an invaluable tool in the operation of any treatment system. The use of SCADA systems will decrease the labor associated with the system as operators will not be required to manually operate many system components or collect operational data, and data can be stored automatically without the need to be hand-keyed into a database. However, the level of automation and the associated life cycle costs (versus labor) should be carefully considered during the design process so that a proper balance is reached between manual operator attention and automated control.

The SCADA system consists of several components[1]:

- Field data devices and a communication system
- Programmable logic controller
- Operator interface terminal

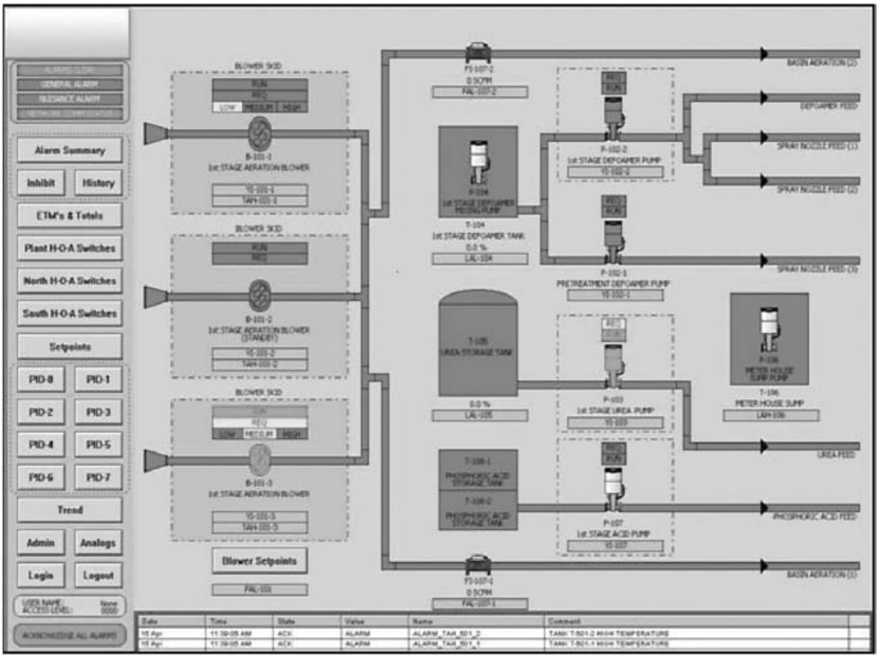
The field data devices consist of instrumentation such as flowmeters, level switches, temperature switches, and pressure gauges. These components provide data to the programmable logic controller, which in turn is used to control the system. The communication system is used to transfer data from the devices to the programmable logic controller.

The programmable logic controller consists of both a hardware and software component that reads the input/output signals from the field devices throughout the plant and is essentially the "brains" of the SCADA system. It can be programmed to provide control of system components, such as the flow of water from a tank in response to a float switch that indicates the tank is full, and data acquisition, such as recording the temperature of the water in the tank at a specified time interval.

The operator interface terminal allows the operator to view operational data and to interface with the SCADA system to control the process (this is what is known as supervisory control). A graphical representation of the system can be developed for use with the operator interface terminal (Figure 7-6). The graphical representation can be used to show operating conditions; for example, if a pump is engaged to run, it can be shown in a green color. It can also be used to present real-time data, such as the flow rate or discharge pressure associated with the pump. In addition, through the operator interface terminal, the operator can be given the ability to override the controls and manually turn the pump on or off as necessary.

Equipment Monitoring and Control

The purpose of equipment monitoring is to provide fail-safe mechanisms to protect from operating conditions that could potentially cause damage or to indicate a general failure in the equipment. For example, a high-pressure switch might be placed downstream of a positive displacement blower. If the pressure increases above the high-pressure set point (indicating a blockage of the outlet piping), it would shut



Date	Time	State	Value	Name	Comment
15 Apr	11:39:05 AM	ACK	ALARM	ALARM_TAH_501_2	TANK T-501-2 HIGH TEMPERATURE
15 Apr	11:39:05 AM	ACK	ALARM	ALARM_TAH_501_1	TANK T-501-1 HIGH TEMPERATURE

FIGURE 7-6. Example of a graphical representation of the SCADA for a treatment system.

down the blower, thus protecting it from potential damage from the high-pressure condition. Another example is utilizing the auxiliary contact on the motor starter to determine if the pump is operational. If the motor starter is engaged to run, but the auxiliary contact indicates that it is not running, either a nuisance alarm will be initiated or, if more appropriate, portions of the system will be shut down.

There is a wide range of equipment for monitoring and control; below are a few of the more common ones:

- Temperature switches
- Pressure switches
- Level switches
- Motor overloads

Any one piece of equipment can be monitored and/or controlled in multiple configurations, and if necessary, redundant fail-safe mechanisms can be used to provide an extra layer of security for critical or costly pieces of equipment, or to reduce the potential for overflows or discharges of untreated water. It is up to the design engineer to determine which configuration is most appropriate for the operating conditions.

Treatment Processes Monitoring and Control

In contrast to equipment monitoring, treatment process monitoring is conducted to allow for automated control of the system, to alert the operator to adverse conditions within the treatment system, or, if necessary, to shut down portions of or the entire system. Examples of treatment process monitoring and control would be the on/off control for a pump utilizing level switches for batch feed from a tank, oxygen monitoring for the control of an aeration blower motor speed using a variable frequency drive, or pH monitoring for the control of acid/base addition.

As with the equipment monitoring, there is a wide range of instrumentation and configurations for monitoring a multitude of parameters. Below are a few of the more common:

- pH meter
- Oxygen meter
- Flowmeter
- Temperature meter

Many field devices can provide both operational control and fail-safe protection by specifying multiple set points in the programmable logic controller.

As with any piece of equipment in a treatment system, instrumentation and other monitoring equipment require regular maintenance to ensure that they are operating as intended. Such maintenance may include simple cleaning, replacement of sensors, regular in-field recalibration, or even recalibration by the manufacturer.

Remote Communications

Remote communication with a treatment plant's SCADA system is becoming more common. Numerous wireless (i.e., satellite or radio) and nonwireless (i.e., cable or telephone) options exist that allow the engineer or system operator to remotely log into the SCADA system and have all the same capabilities as if physically at the plant. The operator can check the status of equipment, observe readings from monitoring equipment, reset alarms, and, if necessary, remotely shut down or restart the system.

The obvious benefit of remote communications is the ability to observe system operation and collect operating data without actually having to go to the site. In addition, the SCADA system can be set up to either call or email the system operator if an alarm condition exists. This allows the operator to respond quickly to an alarm and to get the system operational with as little downtime as possible, whereas without the remote communication, a system could shut down shortly after the operator departs the site, only to be discovered at the time of the next scheduled maintenance and inspection of the system.

PRINCIPLES OF MAINTENANCE

If asked to define what it means to perform maintenance on a piece of equipment, most of us would likely associate it with repairing something that is broken rather than the broader definition of keeping something in good working order. Both definitions are correct, the former would be categorized as corrective or reactive maintenance, whereas the later would be considered preventive maintenance. The goal for any treatment system operation and maintenance program should be to perform the majority of maintenance activities under the preventive maintenance portion of the program, which will limit unnecessary downtime and costly repairs to system components.

No piece of equipment will last forever. Everything in the treatment system will require maintenance at some point in time. Equipment with moving parts will require monthly, quarterly, or yearly maintenance. Tanks and pipes may not require the same frequency of maintenance as equipment but still should be inspected regularly to make sure that something unexpected has not occurred (i.e., silt and sand from the aquifer filling up a pipe or tank). The following sections discuss preventive and corrective maintenance in greater detail, as well as the importance of spare parts inventories and documentation of proper system maintenance.

Preventive Maintenance

Preventive maintenance implies that the equipment or system is serviced and inspected on a regular schedule. Most equipment manufacturers provide recommended inspection and routine service information to their customers, which can be used as a guideline for conducting preventive maintenance. If during an inspection any abnormalities such as vibration or noise are observed, the source of the abnormality should be identified and, if necessary, the component should be repaired or replaced before failure occurs. In general terms, a preventive maintenance program would include the following: inspection and monitoring, repair and replacement, and record keeping. The following discusses the first two topics in greater detail. Record keeping is discussed later in this chapter.

Inspection and Monitoring

It is good practice to implement an inspection schedule immediately following system start-up. Generally, extensive maintenance will not be required during the first six months to one year of operation. The operators should use this period to familiarize themselves with each piece of equipment, its routine maintenance requirements (e.g., changing oil, calibration), and the required frequency and extent of inspections. Depending on the complexity of the system and the intended length of operation, the engineer and/or operator may choose to modify the equipment manufacturer's schedule to be more or less aggressive. However, caution should be used when limiting the maintenance schedule from that recommended by the manufacturer as it may void all or a portion of the warranty provided with the equipment. As an example, for a system that is intended to be in operation for a period of approximately two years, the inspection schedule may be as follows:

Month 1—Weekly inspections follow the system start-up. It is during this period that any "bugs" are worked out of the system, and effective operating parameters are established.
Months 2 and 3—Inspection frequency is reduced to biweekly.
Months 4 to 24—If system has operated reliably, the inspection schedule can be reduced to monthly.

Assuming the system has operated problem free, the temptation may be to reduce the inspection schedule too quickly or to increase the length of time between inspections. It is important to remember that the operating life of the system has likely been established with achieving a regulatory cleanup goal within a specified time period. Extending the life of the project because of equipment malfunction and system shutdown as a result of a lax inspection schedule will not be taken lightly by the regulatory authority and may impose an unnecessary financial burden on the client. The inspection schedule presented above is intended as a general example. Site conditions will ultimately dictate the necessary frequency of system inspection and maintenance. Some conditions that make frequent inspection and maintenance necessary include the following:

- High humidity or wet operating conditions
- High and low temperatures

- Corrosive atmospheres
- Excessive dust and dirt
- High repetitive duty
- Frequent interruptions in electrical service
- Older equipment
- High silt or sand content in the groundwater
- High iron content in the groundwater
- High hardness in the groundwater

An aggressive environment can be particularly detrimental to electrical components. Maintenance on electrical systems and equipment must adhere to the codes and specifications as they apply to the work to be performed. Manufacturers' maintenance instructions, which typically accompany select electrical components, must be applied in conjunction with established electrical codes and specifications such as those listed in the National Electrical Code.[2]

To increase the effectiveness of a long-term system, it is helpful to develop checklists or logs to record data and help evaluate the system operations. The checklist might include the following items:

- General site and system conditions
- Data collection points for process monitoring, including typical ranges for all measurements
- Sampling locations and a list of analytes
- A step-by-step guide for the evaluation of the operation and maintenance of the equipment and processes
- A list of routine maintenance activities and maintenance frequency
- A list of commonly encountered problems and suggestions for corrective action (troubleshooting guide)
- Notes including comments, concerns, or requests from the site owner(s), operator(s), and/or regulator(s).

An example of a simple sampling checklist is shown in Table 7-1. Site-specific checklists should be developed for each system. The checklists should be kept on file throughout the duration of the system operation. A more extensive discussion of record keeping is included in later sections of this chapter.

Repair and Replacement

The timely repair or replacement of components suspected to be damaged or defective is a key element to maintaining reliable and uninterrupted system operation. Unforeseen system shutdowns as a result of failure caused by negligence will result in unnecessary delays in

TABLE 7-1 Example of a System Monitoring Checklist

Sample Location	Sample Name	Analytical Parameter	Analytical Method	Monitoring Frequency	Comments
Air-stripper influent	AS-INF	Volatile organic compounds	8260A	Semiannual	To monitor performance of the remedial system and to evaluate air discharge rates from the air stripper.
System effluent	SYS-EFF	Volatile organic compounds	8260A	Monthly	To monitor performance of the remedial system and for discharge reporting
		Total suspended solids	160.1	Monthly	To monitor performance of the remedial system and for discharge reporting
Individual extraction wells	EW-XXX	Volatile organic compounds	8260A	Quarterly	To monitor performance of the remedial system
Vapor-extraction stack discharge	AS-EFF	Volatile organic compounds	8260A	Quarterly	Required sampling for air discharge monitoring and to monitor performance of the remedial system

achieving project goals. It is imperative that deficiencies noted during routine system operation and inspection be repaired as quickly as possible. An effective way to ensure that repairs are made sooner rather than later is to clearly define responsibility for maintenance. Personnel operating the system must understand that performing routine repairs is part of their scope of work, and they should plan accordingly by having basic tools, spare parts, and test instruments available; planning for assistance for physically demanding tasks; or requesting training they feel is necessary to properly complete tasks. For repairs beyond the technical capabilities of the operator (i.e., electrical repairs), a list of approved vendors/subcontractors should be compiled and provided to maintenance personnel. To this end, it is imperative that routine repair and the replacement of parts be considered during the planning stages of a project to ensure sufficient labor and budget allocations are made.

To minimize downtime during repairs, preventive maintenance must be planned and scheduled. This will help ensure that all necessary replacement parts are available and that the necessary vendor/subcontractor repair personnel are on-site and understand the scope of work prior to shutdown. For repairs or replacement of parts, a lockout/tagout program is essential. This entails making sure the component being serviced or replaced is isolated from the rest of the system if possible (e.g., close valves before and after component), deenergized (no stored energy), and locked out. If isolating the component is not possible, the entire system will need to be shut down. A more detailed discussion of lockout/tagout is presented in the health and safety section later in this chapter.

Corrective Maintenance

Corrective maintenance (or reactive maintenance), refers to repairs performed after equipment failure. Equipment failure typically means mechanical, structural, or electrical failure, but it can also include performance failure as a result of poor design (e.g., undersized pump). Corrective maintenance is conducted at unpredictable intervals and is necessary to return the system to a fully operational state as quickly as possible.

To minimize the need for corrective maintenance, it is important to understand the intended operating schedule of the system. If service is to be continuous, an effective preventive maintenance plan, as previously discussed, is essential. Proper record keeping will provide insight into equipment wear and allow the necessary maintenance to be performed prior to component/system failure. Whenever corrective maintenance is required, an analysis should be performed to establish the cause of failure, to determine if the component should be repaired or replaced, and to determine what system modification, if any, can be made to avert future failures.

Spare Parts and Equipment List

When operating a remediation system, it is helpful to maintain a basic inventory of spare parts, especially of equipment that is critical to maintaining operation. The quantity of spare parts kept on hand is often a function of system location. Many replacement parts are readily available at local hardware, electrical supply, or industrial supply stores. If the system is located in a remote area, however, or the part is available only from a specialty vendor, it may be more cost effective to purchase and maintain an inventory of both basic and critical spare parts to minimize downtime during repairs. Basic spare parts that are useful to have on hand can include valves, gauges, meters, piping, tubing, and miscellaneous fittings of appropriate size and material. The stocking of other specialty or long-lead items will need to be determined on a case-by-case basis and is often determined by the budget available for system operation.

For large systems, every attempt should be made to standardize parts of a certain type and size, such as valves, so that a single spare part can be used in multiple locations. This is also true for systems with a large number of extraction well pumps. One pump can be kept on the shelf and utilized as needed, while awaiting a replacement spare pump. Also, for companies that have a lot of small treatment systems (e.g., gas stations), standardizing the design between all of the locations can increase the cost savings on spare parts inventories.

For sites where the expense of maintaining spare parts inventories is prohibitive, a good approach is to have all of the component information readily available. During the design phase, it is useful to prepare an itemized list of all the equipment and appurtenances specified for the system. This list can initially be used for costing purposes but will also be useful during construction and for subsequent operation and maintenance of the system. As with the documentation previously discussed, the list should be modified to reflect as-built conditions after system construction, as well as any significant modifications that are made to the system. At a minimum, the list should include the following information for each component: the name of the manufacturer, the model number, the component name, and basic operating specifications (i.e., model no., manufacturer, centrifugal pump, 3-horsepower, single-phase, 230-volt). It is also helpful to list vendor or manufacturer contact information for each major piece of equipment. This will help maintenance personnel minimize downtime by providing quick access to technical support when troubleshooting or replacing equipment.

Equipment and Process Documentation

To determine the necessary equipment documentation for an effective maintenance program, it is helpful to view the system both by individual component and as one integrated system. Considering each individual system component will aid in identifying those pieces of equipment for which detailed diagrams, such as equipment cut sheets, will be necessary. Cut sheets are typically supplied by the manufacturer and provide mechanical and structural details, as well as operating parameters for each individual system component. If the equipment has an electrical component, wiring diagrams should also obtained from the manufacturer and made readily accessible.

Having identified the necessary documentation on an individual component basis, the system as a whole should be considered. At a minimum, the following three types of diagrams should be included in the operation and maintenance manual: a process flow diagram, a site layout diagram, and a piping and instrumentation diagram. In addition, a set of as-built drawings should be maintained at the treatment system site for reference purposes.

The process flow diagram is a simplified representation of the system. The process flow diagram shows the treatment train using industry standard equipment shapes and flow direction lines and is intended to allow the reviewer to obtain a quick understanding of the treatment process (Figure 7-7). To this end, the process flow diagram should contain sufficient detail so that the treatment strategy is conveyed without getting into the minutia. The approximate level of detail on a process flow diagram includes the following: system components should be identified with basic specifications (e.g., 250-gallon poly tank); flow direction should be indicated between components; influent and effluent flow rates should be indicated; if flows are split, that split should

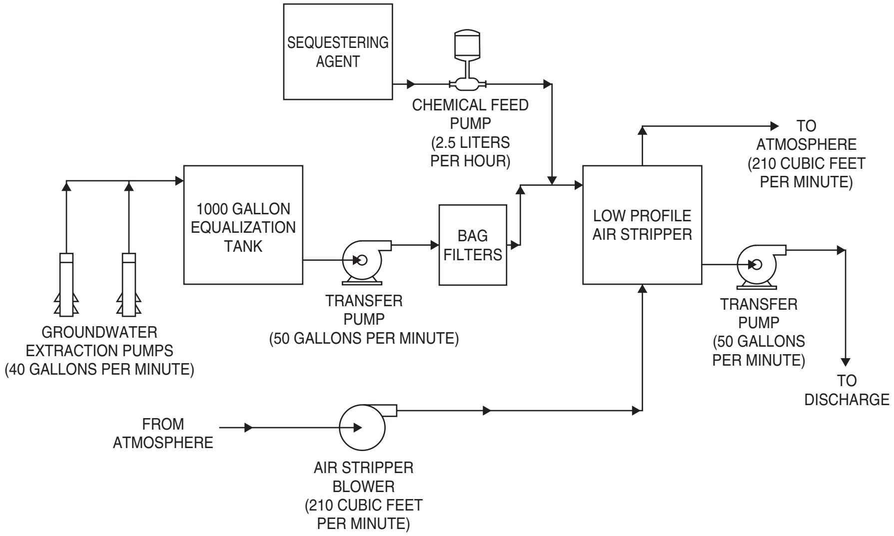


FIGURE 7-7. Example of a process flow diagram.

be indicated on flow lines; final destination should be indicated on the effluent/discharge/waste flow lines (i.e., to sewage treatment plant, to landfill).

In conjunction with the process flow diagram, a site layout diagram is a necessary tool. The site layout diagram is typically a plan view (from above) showing the location of the system components (represented in a manner similar to that in the process flow diagram) and is often referred to when planning system construction or modification. In addition to the system components, the site layout diagram should include the location of utilities, nearby buildings, roads, enclosures, and any other geographic features that may impact the operation of the system. To aid the reviewer with the size and orientation of the system, the site layout diagram should reference north and should include a scale.

With a process flow diagram and a site layout diagram in place to convey a broad view of the system, a piping and instrumentation diagram should be prepared and included as part of the maintenance manual to provide a greater level of detail. The piping and instrumentation diagram provides information on the integration of all the individual components of the system in terms of piping, wiring, controls, sensors, switches, and safeguards. Where the process flow diagram provides very basic component information, the piping and instrumentation diagram includes specific details for each piece of equipment and graphically represents placement of control and interface devices (sensors, switches, gauges, valves, etc.) and the connections between them. The level of detail should be sufficient to provide the reviewer a thorough understanding of the system operation logic, thus providing maintenance personnel an effective troubleshooting tool.

The process flow diagram, site layout diagram, and piping and instrumentation diagram are typically prepared during the design process and are used as guidelines during system construction. More often than not, at the conclusion of the construction phase, some of the system details will have been modified for any number of reasons, such as to allow for space constraints, addition or deletion of components, equipment availability, or changes in system operation strategy. For this reason, it is vital that the process flow diagram, the site layout diagram, and the piping and instrumentation diagram be updated to reflect all changes so that they are an accurate representation of the system (i.e., an “as-built” diagram). Each time a modification is made to the system, the diagrams should reflect that change to ensure that maintenance personnel have accurate as-built diagrams.

RECORD KEEPING AND REPORTING

When discussing preventive maintenance, we briefly discussed the use of checklists and logs to record operational data and to remind the operator of inspection and maintenance tasks that are to be completed. The importance of accurate record keeping cannot be overemphasized. The information gathered over the operating life of the system can be useful in performing trend analyses of the reliability of individual components and of the system as a whole. It is also valuable information to have for optimizing the system, planning system modifications, or designing future systems. Finally, it will be necessary to report portions of these data to the regulatory agencies. Having a complete set of operations data available in an organized manner will aid in the efficient production of the periodic reporting documents.

Record Keeping

Record keeping is an important part of an effective operation and maintenance program. At a minimum, the records that should be kept include operating logs (i.e., operating parameters, settings, flow rates, pressures, temperatures, and run times), equipment inspection and repair logs, and laboratory and field analytical data. The various records should be kept together, be accessible to operating personnel, and be stored in a location protected from the weather. As a precaution, copies should be made of all records and kept in a safe place separate from the originals.

System Operation Logs

An operating log should be maintained and updated during each site visit to record the necessary operating parameters. During the design phase, it is important to consider the level of instrumentation necessary to provide the operator sufficient information to establish and maintain optimum operating parameters. These parameters are initially based on manufacturers' recommendations (i.e., pressure drop across a filter, and air flow rate through a stripper); however, each system is different and may require unique operating criteria. It is imperative that the individuals responsible for operating the system understand the operational constraints (pressure, temperature, flow rate, etc.) not only of each component but also of the system as a whole so that abnormalities can be readily identified.

A well-maintained operational log is critical to successful treatment system operation as it allows the operator to establish trends in the operating parameters that in turn can be used, if necessary, to adjust the maintenance schedule. If, for example, an extraction well's groundwater recovery rate is initially 100 gpm at a pressure of 10 psi and in three months the groundwater recovery rate has decreased to 60 gpm at an increased pressure of 15 psi, it could be an indication of silt accumulation in the lines. The operator may decide to have the lines cleaned, then modify the pumping rate to see if less silt is recovered. This would be an example of an operational change. It may be that the silt recovery is not diminished, and the lines require cleaning after another three months. The operator may then decide to set a quarterly cleaning of the system lines as part of routine maintenance as he continues to troubleshoot the system to understand the root of the problem. Whether or not an ultimate solution is determined, the operator must keep the extraction system running to see that the remediation schedule stays on track.

Equipment Maintenance Records

Equipment maintenance records should be kept on every individual system component that requires servicing, as well as for the system as a whole. For individual components, records should include detailed information such as scheduled maintenance and inspection requirements, any observed deficiencies, repairs performed, and any other related information that would facilitate analyzing the equipment performance. This is applicable to major system components such as pumps, blowers, strippers, product separators, air compressors, tanks, and filters. For the system as a whole, observed deficiencies should be noted and scheduled for repair or replacement. Examples include but are not limited to cracked pipes, leaky valves, broken or defective gauges, damaged electrical wiring, burned out indicator lights, and broken switches. Maintenance records should be retained on file for as long as necessary to allow the collection of sufficient data to perform a system evaluation. This will be helpful in establishing trends to help identify and correct any problem areas on the existing or future systems.

Laboratory and Field Analytical Data

To monitor the effectiveness of the treatment system, samples of the various media from the system (water, air, sludge, etc.) will be collected for analysis. This analysis is typically completed by submitting the samples to an appropriately qualified off-site laboratory but may also be completed utilizing field test kits that analyze for specific parameters. These samples may be collected from various locations within the system, including the influent stream, effluent stream, individual extraction points, and even various points within the treatment process.

Prior to starting the system, a sampling plan should be prepared, outlining sample locations, sample frequency, and sample analyses. This information should be placed in a table format so that it can be readily reviewed and utilized by the system operator. After the sample is collected by the operator and the results are returned by the laboratory, it is recommended that an electronic database be used to store the data as a large quantity of data will be generated over the life of the system. Qualified database operators can then search, sort, and present the data in multiple tabulated and graphical forms. Standardized reporting forms that can be quickly populated by the database operator each time regulatory reporting is required, can also be created.

Reporting

The regulatory agency responsible for oversight of the remediation may require that certain operational and analytical data be submitted on a routine basis. Often agencies have standard reporting forms and checklists that must be completed and submitted on a routine basis to ensure that all of the required data are properly submitted. If a form and checklist are not provided by the agency, it is recommended that a checklist be created to ensure that all required data are submitted and that consistency is maintained throughout system operation. Typical data required in routine reporting may include the following:

- Total system throughput during the reporting period
- System effluent and influent concentrations
- Cumulative mass removal for system
- Number of days of operation during reporting period or percent utilization
- Explanation for extended periods of downtime

Additional data will likely be required, such as contour maps for groundwater plumes or operational data specific to the type of treatment being utilized. The agency with regulatory oversight should be consulted regarding reporting requirements during the design of the system so that appropriate sampling ports and monitoring equipment can be put in place prior to system start-up.

SYSTEM EVALUATION AND OPTIMIZATION

In previous sections, we've discussed the importance of long-term maintenance and record keeping to the overall success of a treatment system. Another integral component is the routine evaluation of the treatment system data to ensure that the treatment system is operating under optimal conditions and that it is effectively meeting the treatment objectives that have been established. This process can be used to identify and correct deficiencies in system operation and to realize opportunities for cost savings over the life of the project.

The system is evaluated based on the data and observations made during routine maintenance and inspection. Typical data used in the evaluation of a treatment system include the following[3]:

- Operational data such as flow rates, pressures, groundwater elevations, and temperatures
- Operational history such as frequently maintained or replaced equipment, power usage, consumable usage, and secondary by-product generation and disposal
- Visual inspection data such as the presence of silt, scaling, or biofouling, pitting or wear on pump impellers, leaks, and the general condition of system components
- Analytical data such as influent and effluent concentrations and individual extraction and monitoring well data

After these raw operational data have been collected, they must be put into a format that allows the data to be easily evaluated. Some of the common tools used for evaluation include the following:

- Graphs of various operational data over time, including total throughput, mass removal, influent and effluent contaminant concentrations, and groundwater elevations
- Monthly summary of power consumption and consumable usage
- Monthly summary of by-product generation (i.e., sludge) and disposal costs

Not all of the data can be easily summarized by a graph, such as general observations made during the operation of the system or information noted on repair logs. However, this information is important to the evaluation process and should be incorporated in any comprehensive review of a treatment system.

After the data have been tabulated and evaluated, recommendations should be made for optimizing the system. These recommendations will be specific to the individual treatment system, but they can generally be categorized as either minor modifications (e.g., adjusting flow rates or chemical additions) or the addition, removal, or replacement of components (e.g., taking redundant equipment off-line or discontinuing off-gas treatment if no longer necessary).[4]

TREATMENT SYSTEM ROLES AND RESPONSIBILITIES

The successful operation of a remediation system is dependent not only on the basic design of the system but more importantly on the operating capabilities of the individuals running the system. If the technical design and approach are flawless but the system is not operated properly, the final remediation goal will not likely be achieved. For this reason, it is important to maintain linkages between the design, implementation, and operation teams throughout the process: from design, through construction and start-up, and, finally, operations.

Responsibilities During Design

The design engineer is responsible for providing a system that can effectively implement the technological approach selected to meet the remedial goal. Care must be taken to make sure that the system, while capable of achieving the desired cleanup goals, makes sense. That is, it can be built and maintained within the allotted budget; the components comprising the system are readily available; replacement parts can be obtained within a reasonable amount of time for a reasonable cost; and the system is not unnecessarily complicated (i.e., keep it simple). System operators may not have the same education and experience as the design engineer; therefore, the system must be designed so that the operation of the system is intuitive. It is also the design engineer’s responsibility to ensure that the system is constructed according to the design by making periodic visits during the construction phase. Additionally, it is a common practice for the design engineer to conduct a formal operational instruction program that covers the actual operation of the equipment and the overall system goals.

Responsibilities During Construction

The construction of a remediation system requires coordination between the design engineer, the construction contractor, and the system operators. The design engineer, or his designated representative, is responsible for making sure that the detailed designs and specifications of materials, equipment, and construction are followed. The engineer overseeing construction must also witness the operation of the equipment after installation and be satisfied that, mechanically, the system operates as it was intended. Special precautions must be taken to eliminate the possibility of the contractor or subcontractor improperly operating any of the system components and causing damage to the system. One example would be the introduction of backwash water into a filter at a rate sufficient to displace the filter medium. This type of problem can be minimized by specifying in the construction contract that equipment operation/testing should be performed only in the presence of, or by, the engineer.

It is the primary responsibility of the construction contractor to complete the remediation system in accordance with all bid specifications and engineering plans within the allotted time. The contractor should also provide a guarantee period, during which he is responsible for the satisfactory operation of the system. This assures that any malfunction that occurs is not the result of negligence or improper operation.

The system operator(s) will be responsible for the operation of the equipment after construction is completed by the contractor. The transition between construction and operation is facilitated by including the operators in the design/build phase of the project. It is especially important to include the personnel responsible for the system while the equipment is being tested. This allows the operators to become familiar with the system and to learn some of the potential difficulties that may be encountered when placing the system in service.

Responsibilities During Operation

The ability of the remediation system to effectively treat the focus medium (i.e., air, water, soil) for which it is designed is the joint responsibility of the design engineer and the system operators. If the system is designed to achieve specific goals but is not operated properly, the results will be unsatisfactory. It is the design engineer's responsibility to provide an operations and maintenance manual and the necessary training to the system operators to ensure that it is operated properly. It is the responsibility of the operators to learn and follow the proper operating protocol and to consult with the design engineer in the event of any malfunctions.

Saying all of this, the main reason that most treatment systems fail to operate properly is lack of maintenance on the moving components of the system. No matter how good the design is, and how well the operators are trained, if the operators do not include maintenance in their schedule, the system will not work over the long term. One classic problem is that operators are not given enough time to maintain the system. When the owner only spends enough on operations to complete the daily requirements of treatment and no expenditures on maintenance, then the system will not work over the long term.

Health and Safety

The most important consideration when performing system operation and maintenance is the health and safety of the operating personnel. Potential hazards associated with a typical remediation system include physical, mechanical, thermal, electrical, environmental, and chemical hazards. Examples of common hazards associated with each of these groups are presented below:

- *Physical*—Piping (overhead and on the ground), ladders, containment walls, lines/hoses (power lines, air lines, water lines), and wet surfaces. These represent typical slip, trip, and fall hazards.
- *Mechanical*—Moving parts on pumps, blowers, mixers, generators, compressors, tanks, and other equipment. Pressurized lines (air, water) and tanks.
- *Thermal*—Hot surfaces on motors, pumps, system piping, generators, and compressors.
- *Electrical*—Equipment wiring, control boxes, breaker panels, and overhead/buried electrical lines.
- *Environmental*—High ambient temperatures, freezing temperatures, confined spaces, spiders, snakes, wasps. All manner of creatures seek the warm and cozy environment provided by your system and enclosure.
- *Chemical*—Chemicals used for system operation (i.e., acid/caustic for pH adjustment), chemicals recovered by the system in either liquid (i.e., free product and groundwater contaminants) or vapor-phase constituents.

A well-maintained system will lead to less potential for dangerous operating conditions that may endanger the operating personnel. The operator should be properly trained to identify and handle hazardous conditions within the system operations and be given the time and budget to conduct all repairs necessary to abate the potential health and safety risk.

A comprehensive health and safety plan should be implemented for every site. The plan should include a discussion of general site safety hazards; the roles and responsibilities of each team member; a hazard evaluation, including a hazard communication section and a hazard analysis for all major tasks to be completed as part of routine and nonroutine operation; and emergency planning details such as the route to the nearest hospital. In all instances, administrative or engineering controls should be used to abate the potential risk from any activity conducted on-site.

Of special consideration for treatment systems is the utilization of lockout/tagout procedures whenever conducting repair or, if applicable, inspection work. The purpose of lockout/tagout procedures is to protect workers from injury by the unexpected and unrestricted release of hazardous energy. Sources of hazardous energy include, but are not limited to, mechanical equipment, electrical systems, hydraulic systems, pneumatic systems, chemicals, and thermal hazards. If you service equipment where there is a potential for hazardous energy to be released, the Occupational Safety and Health Administration (OSHA) requires that the equipment must be shut down and isolated from all energy sources.[5] It is also required that lockout/tagout devices must be applied to the energy isolation devices. Finally, all operating personnel should be trained to identify sources of hazardous energy and know how to properly isolate each source in accordance with OSHA requirements.

References

1. National Communication System Technical Information Bulletin 04–1, Supervisory Control and Data Acquisition Systems, October 2004.
2. National Electrical Code (NEC), NFPA 70, National Fire Protection Association, 2008.
3. Interstate Technology & Regulatory Council (ITRC), *Above Ground Treatment Technologies*. RPO-4, 2006.
4. Interstate Technology & Regulatory Council (ITRC), *Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation*, RPO-1, 2004.
5. Occupational Safety and Health Administration (OSHA), Lockout/Tagout Fact Sheet, 2002.

8

Emerging Contaminants

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We have shown in chapters 1 through 7 that significant progress has been made in the knowledge and experience for remediation of groundwater. We know how to get most of the mass out, and then how to follow up with natural and enhanced biological systems to destroy the organic contaminants controlled by the geological limits of the aquifer.

While we know how to take care of 99 percent of the organic chemicals, during the last several years, we have discovered several organic and inorganic compounds that are not easily remediated by these techniques. The reader should be aware of the limitations of in situ remediation techniques when dealing with the following organic compounds: MTBE; 1,4-dioxane; perchlorate; *n*-nitrosodimethylamine; arsenic; hexavalent chromium; and 1,2,3-trichloropropane.

There are several problems in dealing with these compounds from a remediation perspective. First, most of them have not been part of the list of organic compounds that are requested to be analyzed by the laboratory. Some show up on the tentative identified compound (TIC) list, some are not recognized by standard analytical methods, and some have only recently had an analytical method for low parts per billion µg/L) or low parts per trillion (nanograms per liter, ng/L) detection. Second, these compounds are, in general, very soluble, have low retardation in the aquifer, and are relatively slow degraders. This combination of properties creates large plumes of organic or inorganic contaminants that move very close to the speed of the aquifer. These two problems have combined to create situations in which we have organic or inorganic compounds that are just recently being regulated and have not been detected in our standard groundwater analysis but are present. This means that on some new sites and on some sites that have already been cleaned and closed there are large plumes of newly regulated compounds.

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The final problem with these compounds is that their physical, chemical, and biochemical properties prevent the use of most of the remediation methods discussed in this book. Most sites that have found these compounds have had to rely on pump and treat as their control and remediation method. Even when brought aboveground, the treatment methods for these compounds have proven to be very expensive.

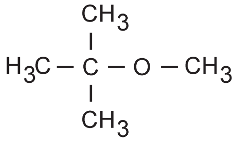
We review the history, physical and chemical properties, and remediation methods of each of these compounds. This will prepare the reader for the types of sites that should be tested for the presence of these compounds.

METHYL TERTIARY BUTYL ETHER AND OTHER FUEL OXYGENATES

Background and History

MTBE is a compound that was adopted in the 1980s to serve two purposes as a gasoline additive: to enhance the octane rating for gasoline and to provide oxygen to boost combustion efficiency. MTBE's octane-enhancing quality led to its approval as an oxygenate in 1979. It substituted for the alkylated lead compounds that were being phased out. Oxygen contained in MTBE also increases combustion efficiency, reducing carbon monoxide emissions. In 1981, the U.S. EPA approved MTBE's use in gasoline up to 10 percent by volume. It was used in higher percentages in premium gasoline than in regular gasoline. The first winter oxygenated gasoline program in the nation was implemented in Denver, Colorado in 1988.[1] This trend expanded to other states as regulatory agencies attempted to reduce cold-weather vehicular emissions.

Starting in 1992, in 15 or more states, the Clean Air Act required that gasoline contain oxygenates to reduce carbon monoxide emissions in nonattainment areas. Up to 17 percent MTBE was used to achieve the



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

METHYL TERTIARY BUTYL ETHER
(MTBE)

FIGURE 8-1. Methyl tertiary butyl ether (MTBE).

required oxygen content. Although other oxygenates could have been used, MTBE was used the most because of its compatible qualities. The federal reformulated gasoline (RFG) program, starting in January 1995, resulted in up to 15 percent MTBE (11 percent in California) being added to gasoline to provide 2.7 percent oxygen.[2] With the expansion of oxygenate use under these programs, 30 or more percent of the gasoline sold in the United States contained oxygenates.[3]

Federal RFG was adopted in 28 metropolitan districts throughout the United States. Its use was primarily intended to decrease the production of ozone, and it was required year round. Federal RFG was required to contain at least 2 percent oxygen from any oxygenate during the summer season. The demand for MTBE resulted in an unprecedented rate of production growth. In the early 1970s, its production was about 12,000 barrels per day, or the 39th highest produced organic chemical in the United States. By 1998, it had become the fourth highest and was produced at about 250,000 barrels per day.[3] In 1998, more than 10.5 mgd were being consumed in the United States and 4.2 mgd in California.[4] Production of MTBE peaked in 1999 and has steadily declined since as states have adopted more stringent regulatory standards for MTBE, and many have passed legislation to phase out the use of MTBE altogether. At least 25 states have instituted a partial or complete ban on the use of MTBE as a fuel oxygenate. Table 8-1 lists the states, the proposed date of the action, and the proposed action.

In 2005, the U.S. EPA removed the 2-percent oxygenate requirement from RFG. The removal was in direct response to environmental concerns over the release of MTBE into the environment from leaking underground storage tanks and their ancillary equipment. The phase-out of MTBE in RFG had already begun back in 2001 as several states sought legislation to ban the use of MTBE as a gasoline additive. As a direct result, MTBE production has decreased in the United States to approximately 140,000 barrels per day. Alternative oxygenating compounds are now taking the place of MTBE, with the most prevalent being ethanol. In 2005, approximately 255,000 barrels per day of ethanol were being used to produce gasoline in the United States. As ethanol production capacity increases, it is likely that it will completely replace MTBE as a fuel oxygenate.

Methyl Tertiary Butyl Ether Characteristics

In addition to its functional characteristics being a benefit to gasoline, MTBE's chemical and physical characteristics made it a desirable additive. MTBE is miscible in gasoline and is not hygroscopic. This

TABLE 8-1 State Actions Banning Methyl Tertiary Butyl Ether

State	Effective Date	Extent of MTBE Ban
Arizona	January 1, 2005	0.3% max volume in gasoline
California	December 31, 2003	Complete ban in gasoline
Colorado	April 30, 2002	Complete ban in gasoline
Connecticut	January 1, 2004	Complete ban in gasoline
Illinois	July 24, 2004	0.5% max volume in gasoline
Indiana	July 24, 2004	0.5% max volume in gasoline
Iowa	July 1, 2000	0.5% max volume in gasoline
Kansas	July 1, 2004	0.5% max volume in gasoline
Kentucky	January 1, 2006	0.5% max volume in gasoline
Maine	January 1, 2007	0.5% max volume in gasoline
Michigan	June 1, 2003	Complete ban in gasoline
Minnesota	July 2, 2005	Complete ban in gasoline (following partial ban in 2000)
Missouri	July 1, 2005	0.5% max volume in gasoline
Montana	January 1, 2006	No more trace than trace amounts in gasoline
Nebraska	July 13, 2000	1% max volume in gasoline
New Hampshire	January 1, 2007	0.5% max volume in gasoline
New Jersey	January 1, 2009	0.5% max volume in gasoline
New York	January 1, 2004	Complete ban in gasoline
North Carolina	January 1, 2008	0.5% max volume in gasoline
Ohio	July 1, 2005	0.5% max volume in gasoline
Rhode Island	June 1, 2007	0.5% max volume in gasoline
South Dakota	July 1, 2001	0.5% max volume in gasoline
Vermont	January 1, 2007	0.5% max volume in gasoline
Washington	January 1, 2004	0.5% max volume in gasoline
Wisconsin	August 1, 2004	0.5% max volume in gasoline

Source: This table is adapted from the U.S. EPA (2004) and McCarthy and Tiemann (2005). It has been further updated as more recent information has become available in the media. For current information, see individual State regulations.

is not true for alcohols, as they tend to absorb water and have limited anhydrous solubility. When alcohols absorb water, the tendency to break phase is increased. MTBE is also relatively inexpensive to produce as it is synthesized from isobutene, a by-product of petroleum refining. The majority of MTBE used in the United States comes from local sources, with the remainder being imported.

Table 8-2 summarizes the physical and chemical characteristics of MTBE. The normal boiling point of MTBE, 55°C, and its vapor pressure of 254 mmHg at 25°C is compatible with the mixture of hydrocarbons in gasoline (benzene vapor pressure is between 76 and 95 mmHg). Thus, it can be successfully transported by tank or pipeline. The aqueous solubility of pure MTBE is higher than any other gasoline component, 43,000 to 54,000 mg/L[1] Under these conditions, its aqueous solubility has been determined to be 4,700 mg/L from RFG containing 11.1 percent MTBE, and 6,300 mg/L from oxyfuel containing 15 percent MTBE. These compare with 18 mg/L for benzene

TABLE 8-2 Physical and Chemical Properties of Methyl Tertiary Butyl Ether

Characteristic/Property	Data
Formula	$C_5H_{12}O$
Molecular weight	88.15 g/mol
Specific gravity	0.745
Water solubility (ppm)	51,000 ppm
Log K_{ow}	1.24
K_{oc}	11.2
Henry's law constant (atm)	32.6
Vapor pressure (mmHg at 25°C)	254

Source: Nyer et al. (2001).

and 25 mg/L for toluene dissolving from gasoline in equilibrium with water.

MTBE is chemically stable as an ether, and because the tertiary butyl structure provides steric hindrance, it is also resistant to biodegradation. Acclimated bacterial populations under controlled conditions, ex situ, show some promise with biodegradation, but in situ intrinsic attenuation has had limited success. Partial degradation products such as TBA are also contaminants in their own right. The high solubility of MTBE, coupled with its resistance to chemical destruction or biodegradation, results in its being highly mobile in groundwater and subject to very little retardation. The observed retardation factors for MTBE in soils with 0.1 percent organic carbon and 0.4 percent organic carbon are 1.09 and 1.38, respectively. This compares to 1.75 and 3.99 for toluene under the same conditions. These factors led to the observation that MTBE is the compound most likely to be found at the leading edge of a contaminant plume originating with gasoline.[5]

MTBE is difficult to treat because it resists air stripping, adsorbs poorly on activated carbon, and resists biodegradation. These treatment technologies are relatively effective for the hydrocarbon compounds that act as gasoline contaminants, predominantly BTEX. Thus, MTBE may survive standard treatment technologies for hydrocarbons and cause the treated effluent to be out of compliance with discharge standards in pump-and-treat systems.

Regulatory Framework

After MTBE was authorized as a gasoline additive by the U.S. EPA, its use was slowly increased as an octane enhancer. The 1990 Amendments to the federal Clean Air Act mandated that oxygenates be incorporated in gasoline sold in regions that failed to comply with federal air quality standards. For reasons previously discussed, MTBE became the oxygenate of choice for the petroleum refining industry.

The positive air quality benefits accruing from the use of MTBE have been somewhat offset by public and regulatory concerns over its presence as a groundwater contaminant and its potential threat to public health. Both the public and regulatory agencies have held differing views of the risks to public health and the environment associated with MTBE. Some regard it as a toxic contaminant of concern, while others regard it as a low-risk contaminant. As a result, regulations covering MTBE from state to state are fractured.

In the United States, 25 of the 50 states have some form of drinking water standard for MTBE. Eleven states have adopted the U.S. EPA's drinking water advisory level (between 20 and 40 μg/L]), and 13 states have established health advisory levels of their own. The standards range from nondetectable (Kansas) to as high as 240 μg/L (Michigan), with the vast majority of standards at or below 20 μg/L.[6] Table 8-3 summarizes the state-by-state regulatory status of MTBE as of March 2005.

It is evident that state responses to MTBE both as a potential and active contaminant range from banning the compound, as is the case for six states, to regarding it as a low-toxicity substance indicative of contamination by more toxic compounds.

TABLE 8-3 State Primary Drinking Water Standards for Methyl Tertiary Butyl Ether

State	Primary Drinking Water Standard (μg/L)
California	13
Colorado	15
Delaware	10
Maine	35
Mississippi	240
Missouri	20
New Hampshire	13
New Jersey	70
New York	50
Oregon	20
Vermont	40

Source: NEIWPCC (2003).

Note. Two additional states, Illinois and Kansas, are listed by NEIWPCC as having primary drinking water standards, but apparently in error, as no numerical value for either standard is provided. Because this table is based on information collected in 2003, it may not be current. For the most up-to-date information and complete details, see state regulations.

The U.S. EPA, under the Safe Drinking Water Act, as amended in 1996, published a list of contaminants that were not subject to any proposed or promulgated national primary drinking water regulation at the time of publication, are known or anticipated to occur in public drinking water systems, and may require regulations under the Safe Drinking Water Act. This list, the Contaminant Candidate List, was published in final form March 2, 1998.[7] A second Contaminant Candidate List was published in February 2005 and carried forward 51 items, including MTBE, from the original list. The Contaminant Candidate List includes contaminants identified as priorities for drinking water research, contaminants that need additional data on the frequency of occurrence, and contaminants for which development of future drinking water regulations and guidance is justified.

The U.S. EPA is presently advising that MTBE concentrations in drinking water be limited to a range of 20 to 40 μg/L to prevent taste and odor problems and to protect human health.[8] MTBE is odoriferous, with a reliable organoleptic threshold of 5 μg/L. Heating contaminated water for cooking or bathing increases the odor intensity and vaporization.

Environmental Behavior and Fate

Characterizing groundwater contaminant plumes originating with MTBE-containing gasoline requires some aspects that are common to all groundwater contamination investigations and some aspects specific to dealing with MTBE or other fuel oxygenates in general. Fundamentally, the groundwater regime must be characterized in regard to groundwater flow direction, velocity, and tendency for an upward or downward component of flow. The migration of MTBE will follow the flow regime at a velocity approaching the groundwater velocity.

MTBE sources and fuel hydrocarbon sources, as evidenced by dissolved plumes, may not be the same. Because hydrocarbons are subject to relatively high biodegradation and retardation in the subsurface, and MTBE is not, a greater mass of hydrocarbons is required to create a contamination zone. For example, a small leak in the dispensing system at a service station could release MTBE-containing gasoline that would produce an MTBE plume without accompanying hydrocarbons. Vapor-phase transport of MTBE in soil might also result in displacement of the apparent location where the MTBE enters the groundwater system. The light hydrocarbon compounds are not as likely to exhibit this behavior as their vapor pressures are lower and their aqueous solubilities are even lower (see the Methyl Tertiary Butyl Ether Characteristics section above).[5]

A United States Geological Survey (USGS) study[9] has suggested that low-level MTBE contamination found in outlying surface waters in New Jersey may be the result of atmospheric deposition. Because of the high volatility of MTBE and its relative solubility, the compound is believed to be transported in the air and then deposited during rain events. Another USGS study[10] concludes that low-level MTBE contamination in the northeast United States is probably attributable to a combination of atmospheric deposition, small surface spills, and storm-water runoff.

MTBE is a unique component of gasoline because of its relatively high aqueous solubility and resistance to biodegradation. Natural attenuation is a process that is almost universally applied to the chemical components of gasoline when it is released into the groundwater environment. Bacteria that are present in the subsurface, particularly when conditions are aerobic, are able to metabolize the hydrocarbon compounds, thereby reducing their concentrations through biodegradation.[11] Many locations have been documented where the migration of hydrocarbons from the source area reaches a point downgradient where their migration rate and degradation rate balance, and the plume stabilizes. The presence of MTBE complicates plume management because it either does not biodegrade or biodegrades so much more slowly than the other hydrocarbons that it persists, creating a contaminant plume of its own. Some public supply wells have become contaminated with MTBE in the absence of other gasoline hydrocarbon components.

As noted in the Methyl Tertiary Butyl Ether Characteristics section, its solubility is approximately 20 times that of benzene, the next most soluble component. MTBE's solubility and nonpolarity result in its moving relatively unimpeded by adsorption or ionic attraction to the aquifer soil matrix when it occurs in groundwater. It, therefore, acts essentially as a conservative tracer, moving at the velocity of groundwater. This flow characteristic allows MTBE to migrate ahead of the other gasoline hydrocarbon components as they disperse into groundwater. The resulting plume, after moving a distance downgradient, will show MTBE at the leading edge. Because its biodegradation is very slow, as previously discussed, MTBE may be found as the sole component in the advancing plume. At this stage, the other hydrocarbon compounds will have reached a stabilized position of input and degradation behind the MTBE.

Treatment Options

Adsorption

Many contaminants can be effectively removed from water and air by GAC. GAC is manufactured from a variety of carbon sources, including bituminous and lignite coal, wood, and coconut shells. The goal in manufacturing an activated carbon is to create a pore structure within the carbon particle that provides a large adsorption surface, the more "high-energy" pores that are produced, the more effective the GAC will be toward "weakly" adsorbing compounds. Weakly, moderately, and strongly absorbing compounds are a function primarily of the compound's aqueous solubility and concentration. Relatively soluble compounds such as MTBE and other fuel oxygenates fall into the weakly adsorbed category. GAC with the most high-energy pores is derived from coconut shells. Lignite coal- and wood-based GAC typically have a low percentage of high-energy pores and therefore do not perform well in removing MTBE from water.

Recently, a bituminous coal-based GAC was introduced that is manufactured from select grades of coal and is optimized with a high percentage of high-energy pores. Testing has shown it is capable of sorbing 0.24 grams per 100 milliliters (g/100 mL) at 100 μg/L MTBE compared with standard bituminous coal at 0.12 g/100 mL or coconut shell at 0.09 to 0.20 g/100-mL.[12] The bed life for this product should be longer, reducing carbon exchanges, downtime, and treatment cost.

Air Stripping

Air stripping is a standard treatment technique for VOCs in water. Numerous groundwater contamination problems have been caused by petroleum products containing VOCs or synthetic organic solvents that are volatile. Air stripping efficiency is based on Henry's law constant, which is a mathematical value based on a combination of the compound's volatility and aqueous solubility. High volatility gives a high Henry's law constant, whereas high aqueous solubility reduces the Henry's law constant. For example, benzene has a high Henry's law constant of 230 atmospheres fraction, and MTBE, with a higher vapor pressure, has a value of 32.6. This difference in Henry's law constant requires that an air-to-water ratio of up to 10 times higher be used to strip MTBE than is needed to strip BTEX hydrocarbons. Since air stripping is not a destructive treatment technology, the resulting effluent vapor stream may require additional treatment to remove MTBE or other fuel oxygenates.

Air Sparging

Air sparging can be used to treat MTBE and other fuel oxygenates in situ. However, as with air stripping, because of their low Henry's law constants and high solubility in water, they will require a much higher air injection flow rate than BTEX compounds. Alcohol-based fuel oxygenates require approximately 100 to 1,000 times more sparge airflow than BTEX, and ether-based fuel oxygenates like MTBE require 10 times more airflow than their alcohol-based counterparts (or 1,000 to 10,000 times more airflow than BTEX compounds).[13] Because of the high volume of sparge air required, air sparging alone may not be the most cost-effective treatment technology for MTBE and other fuel oxygenates, but it may be effective if used in conjunction with other treatment technologies (e.g., soil vapor extraction, pump and treat, etc.). Air sparging is generally not effective for treating groundwater contaminated with TBA.[14]

Biodegradation

MTBE and other fuel oxygenates do not biodegrade as readily as BTEX compounds, but they can be aerobically degraded (anaerobic pathways also exist, but they have been confined to laboratory studies that have been inconsistent). Because oxygenate-degrading microorganisms are typically slow growing, bench-scale and pilot-studies may be required to determine if bioremediation can be effectively implemented at a specific site.

Biodegradation has been shown to produce TBA, a compound also regarded as a contaminant.[11] Recent research has found that most bacteria that degrade MTBE are obligate aerobes, which means all of the hydrocarbons must be degraded first so the source of oxygen demand is removed, and then natural or enhanced oxygen must be present for bacteria to degrade the MTBE or other oxygenates. Even under these conditions, biodegradation does not occur at every site.

Most research has focused on the biodegradation of MTBE and TBA, but other fuel oxygenates are suspected to follow similar biodegradation pathways. Ethanol may affect the biodegradation of MTBE and can deplete electron acceptors and stimulate methanogenesis.[13]

In situ bioremediation successfully reduced concentrations of BTEX, MTBE, and TBA concentrations at one site that were $>10{,}000\ \mu\text{g/L}$ in the center of the plume. After 18 months of operating a biobarrier system, downgradient concentrations at a monitoring well were $<5\ \mu\text{g/L}$.[13] This site utilized a 500-foot-wide biobarrier that acted as a passive flow-through system, which was installed downgradient of a NAPL plume. Contaminated groundwater traveled through the biobarrier, which was partitioned into sections; each section was injected with combinations of oxygen, air, and conditioned microorganisms. Each of the partitions demonstrated equal remedial effectiveness. Dissolved oxygen concentrations increased from 1 mg/L before the injections began to 10 to 35 mg/L throughout the treatment zone during active injection. Oxygenate-degrading microorganisms are typically very slow growing; bench-scale and pilot-studies may be needed to confirm the applicability of bioremediation at a site.[13]

The successful use of ORC (oxygen release compound) in reducing MTBE concentration in groundwater from 800 μg/L to less than 2 μg/L at a service station spill site was reported by Koenigsberg.[15] The ORC was injected into the aquifer where BTEX and MTBE were present in dissolved form. The reported reduction in concentration was achieved over a nine-month period. It must be noted that results such as this may not be typical and that aerobic biodegradation of fuel oxygenates generally occurs much more slowly than aerobic biodegradation of petroleum hydrocarbons.

Advanced Oxidation

Advanced oxidation technologies chemically oxidize MTBE and other fuel oxygenates with the hydroxyl radical. One means of generating a hydroxyl radical is with high-energy, medium-pressure UV light to photodissociate hydrogen peroxide into two hydroxyl radicals in a UV reactor. The hydroxyl radical is a powerful, rapid oxidizer—hence the term *advanced* is used to denote the kinetic rate constant that is one million to one billion times faster than other chemical oxidizers, such as ozone. The UV/peroxide process has been implemented at more than 250 sites worldwide for routine removal of organic compounds in drinking water.[16]

Another process that produces the hydroxyl radical is ozone coupled with hydrogen peroxide. This system is used in Europe because of the common use of ozone as a water disinfectant there. If a bromide ion is present in the water, a bromate ion, a suspected carcinogen, may be formed with this process. This type of aboveground treatment is commercially available in the United States. One such system is the HiPOx from Applied Process Technology. This system treated water at a northern California gas station that had concentrations of the following fuel oxygenates: MTBE from 30,000 to 53,000 μg/L; TBA from 3,200 to 9,100 μg/L; and tertiary-amyl methyl ether from 3,000 to 6,200 μg/L. Additionally, this site had BTEX concentrations from 4,500 to 6,500 μg/L, and TPH as gasoline (TPH-g) concentrations of approximately 30,000 μg/L. The HiPOx system treated water at a flow rate of 2.5 gpm, and reduced MTBE concentrations to <5 µg/L, TBA to <100 µg/L, tertiary-amyl methyl ether to <10 µg/L, BTEX to <5 µg/L, and TPH-g to S/B >500 µg/L.[17]

Fenton's reagent generates a hydroxyl radical in a solution with ferrous iron and hydrogen peroxide under acidic conditions. The reaction generates ferrous iron that acts as a catalyst. When Fenton's reagent reacts with an organic substrate, heat is produced. Fenton's reagent destroys BTEX, MTBE, and TPH-g in water under controlled conditions as cited above. When reacted in Tedlar bags enabling off-gases to be collected, MTBE was completely oxidized to carbon dioxide[18]. It can pose problems when it is applied in situ because optimum conditions for the reaction can be difficult to maintain. This technology can quickly reduce concentrations of MTBE and other oxygenates when carefully applied. This technology reduced concentrations of MTBE from 6,400 µg/L to <5 µg/L in three months at a site in New Jersey.[13]

A peroxy-acid process utilizing glacial acetic acid and hydrogen peroxide also generates the hydroxyl radical. In controlled laboratory tests, the MTBE concentration was reduced by 30 percent in two hours.[19] Other recalcitrant compounds, including tetrahydrofuran and 1,4-dioxane, were also degraded by this process.

In Situ Technologies

An inherent problem with any in situ oxidative approach to remediate MTBE, or any other contaminant, is that of competitive reactions. The subsurface environment in most places is one having some degree of reducing conditions. Residual organic matter in geologic materials, reduced iron, manganese, sulfur species, and dissolved natural organic matter all react with oxidants that they contact. This phenomenon is called the reductive poise of a location. The amount of oxidant that is required to react with any or all of these substances must be introduced in order to have excess oxidant available for the target compounds. With moderate to large zones of contamination, overcoming the reductive poise may require hundreds of thousands of dollars worth of reagents and hardware.

In situ chemical oxidation, presented earlier, has been successfully applied at numerous sites. Hydrogen peroxide, ozone, permanganate, persulfate, and other oxidizing compounds have been used individually or in combination to treat MTBE and other fuel oxygenates. These compounds have been introduced into the subsurface by injection through wells, groundwater extraction/amendment/reinjection (i.e., a recirculation system), lance injection (including jetting and fracturing), soil mixing, and by permeable reactive barriers.[13]

Phytoremediation

Tree roots develop a symbiotic population of bacteria, fungi, and actinomycetes in their immediate vicinity, which is termed the rhizosphere. Tree root exudates are organic compounds that are released from the tree roots into the soil. The associated microorganisms metabolize these compounds and, in turn, produce other compounds that are beneficial to the tree. This system becomes a biologically active zone capable of decomposing synthetic organic compounds through cometabolism. The tree roots also may absorb organic compounds where they are fixed in the tree tissue, transported and transpired with water through the leaves, or otherwise metabolized as part of the tree's metabolic activity.

Phytoremediation is performed by planting trees (particularly hybrid poplars because they are rapid growing and transpire a large quantity of water) to interact with soil or shallow groundwater contaminants. When roots reach the capillary zone or the water table, they will transpire a large volume of water. Using radiocarbon-labeled MTBE, poplar trees were shown to remove over 80 percent of MTBE from hydroponic solution within 11 days. When planted in soil, poplars removed more than 55 percent of the MTBE through transpiration, with only 4.75 percent remaining in soil.[20]

A service station site in northern California demonstrated that pine trees may have been inhibiting the off-site migration of MTBE and TBA. Groundwater downgradient of a stand of poplar trees had reduced concentrations of MTBE and TBA. Additionally, transpirate samples collected from the trees had concentrations of MTBE and TBA.[14]

1,4-DIOXANE

Background and History

Recent production data for 1,4-dioxane is not readily available; however, it is a high volume chemical with annual production exceeding one million pounds in the United States. In 1990, the total U.S. production of 1,4-dioxane was between 10,500,000 and 18,300,000 pounds (U.S. EPA, 1995). Production levels are expected to decline as usage patterns change. Currently, 1,4-dioxane is produced in the United States by two manufacturers: Dow Chemical and Ferro Corporation.[22]

1,4-Dioxane is used as a solvent for various applications, primarily in the manufacturing sector. 1,4-Dioxane is used as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, lacquers, plastics, latex,

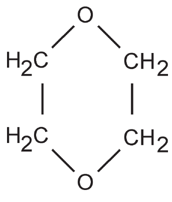


FIGURE 8-2. 1,4-Dioxane.

varnishes, paints, dyes, resins, oils, fats, waxes, greases, and polyvinyl polymers.[23] It is used as a reaction medium solvent in organic chemical manufacturing, as a reagent for laboratory research and testing, as a wetting agent and dispersing agent in textile processing, as a solvent for specific applications in biological procedures, as a liquid scintillation counting medium, in the preparation of histological sections for microscope examination, in paint and varnish strippers, and in stain and printing compositions.[23] 1,4-Dioxane is also used in shampoo, deodorant, fumigants, cleaning and detergent preparations, and automotive coolant liquids. 1,4-Dioxane was also used as a solvent for coatings, sealants, adhesives, cosmetics, and pharmaceuticals, but these uses have been discontinued because of the potential carcinogenicity of the compound.[23]

In 1985, 90 percent of 1,4-dioxane produced in the United States was used as a stabilizer for chlorinated degreasing solvents such as 1,1,1-trichloroethane and trichloroethene.[21] A chlorinated degreasing solvent is a mixture of one or more chlorinated hydrocarbons plus additives that act as stabilizers and inhibitors.[24] 1,4-Dioxane acts as an inhibitor to prevent corrosion of aluminum surfaces. 1,1,1-Trichloroethane typically contains several percent (2 to 3.5 percent) 1,4-dioxane, and trichloroethene may contain small quantities (<1 percent) of 1,4-dioxane.[24] Chlorinated degreasing solvents are used in the process of vapor degreasing, a process that removes oil and grease from the surface of machined metal and nonmetal parts. The oil and grease originates from machining and other fabrication operations that leave machining oils, lubricants, and soldering flux on the surface of the part being cleaned.[24] Wastes generated by the degreasers (still bottoms or sludge) may contain solvent, additives, oil, grease, solids, and water. For example, sludge generated by the degreasers in the aerospace industry typically are composed of 70 to 80 percent solvent and 20 to 30 percent oil, grease, and solids, with traces of water.[24]

Evidence suggests that very soluble additives, such as 1,4-dioxane, tend to concentrate in the still bottoms generated by the degreaser.[25]

It was common practice until the 1970s that the sludge from the distillation process could usually be poured on dry ground away from buildings, and the solvents were allowed to evaporate, assuming there were no special ordinances to prevent it.[24] Sludge or waste solvent that was poured on dry ground and that did not evaporate or was not incinerated would constitute a DNAPL upon entering the subsurface. Because the sludge from the degreasing process contained 1,4-dioxane, sites where 1,1,1-trichloroethane and trichloroethene have been detected in groundwater most likely contain 1,4-dioxane. Because 1,4-dioxane is not included on the U.S. EPA target compound lists or standard laboratory analytical lists, it is likely that this compound may have not have been included on the chemical analyte list for the site.

1,4-Dioxane Characteristics

The physical and chemical properties of 1,4-dioxane are presented in Table 8-4. 1,4-Dioxane is an ether. The functional group of an ether is an oxygen atom bonded to two carbon atoms.[26] 1,4-Dioxane is a cyclic ether, which is a heterocyclic compound in which the ether oxygen is one of the atoms in a ring. Ethers are polar molecules in which oxygen bears a partial negative charge, and each attached carbon bears a partial positive charge.[26] However, only weak dipole–dipole interactions exist between their molecules in the pure state. Consequently, boiling points of ethers are much lower than those of alcohols of comparable molecular weight and are close to those of hydrocarbons of comparable molecular weights.[26] Because the oxygen atom of an ether carries a partial negative charge, ethers form hydrogen bonds with water; therefore, they are more soluble in water than hydrocarbons of comparable molecular weights and shapes.[26] 1,4-Dioxane is

TABLE 8-4 Physical and Chemical Properties of 1,4-Dioxane

Characteristic/Property	Data
Appearance	Colorless liquid
Melting point	11.8°C
Boiling point	100–120°C
Vapor density	3
Vapor pressure	27 mmHg at 20°C
Density	1.034 g/cm^3

Source: Nyer et al. (2001).

miscible in water, which means that this compound is capable of being mixed with water in all proportions. Ethers are resistant to chemical reaction. They do not react with oxidizing agents such as potassium dichromate or potassium permanganate.[26] They are stable toward even very strong bases, and most ethers are not affected by most weak acids at moderate temperatures. Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions.[26]

Regulatory Framework

1,4-Dioxane is regulated by the following federal regulatory programs: the Clean Air Act, Occupational and Safety Health Act, Resource Conservation and Recovery Act, Superfund (CERCLA), and Toxic Release Inventory Chemicals.[27] The Clean Air Act Amendments of 1990 list 1,4-dioxane as a hazardous air pollutant. The Occupational and Safety Health Act final permissible exposure limit (PEL) is 100 parts per million of air (mg/L) as an 8-hour time-weighted average.[28] 1,4-Dioxane is classified as a U108 hazardous waste under the Resource Conservation and Recovery Act.

There are no federal primary or secondary drinking water standards for 1,4-dioxane. 1,4-Dioxane is not included in the Drinking Water Contaminant Candidate List, a list of contaminants the U.S. EPA is considering for possible new drinking water standards; however, this compound was on the Drinking Water Priority list, the predecessor of the Drinking Water Contaminant Candidate List. The U.S. EPA has issued final 1-day and 10-day Drinking Water Health Advisories for 1,4-dioxane for a 10-kilogram child of 4,000 and 400 μg/L, respectively.[29] In the 1987 Drinking Water Health Advisory, the drinking water concentration associated with the 10^{-4} cancer risk was 700 μg/L.[29] In 1990, the drinking water concentration associated with the 10^{-4} cancer risk was updated to a more conservative 300 μg/L.[30]

Because there is no primary maximum contaminant level (MCL) for 1,4-dioxane, concentrations detected in groundwater are generally compared to the U.S. EPA region III risk-based concentration for tap water (6.1 μg/L) or the region IX preliminary remediation goal for tap water (6.1 μg/L) when assessing a site for impacted groundwater. The U.S. EPA region III risk-based concentrations and region IX preliminary remediation goals are chemical concentrations corresponding to fixed levels of risk (i.e., hazard quotient of 1 or a lifetime cancer risk of 10^{-6}, whichever occurs at a lower concentration). The risk-based concentrations were developed by taking toxicity constants (reference doses and carcinogenic potency slopes) and combining these constants with "standard" exposure scenarios.

1,4-Dioxane is regulated under several California State Regulatory Programs, including the California Air Toxics "Hot Spots" Information and Assessment Act of 1987 (Assembly Bill 2588), California Law Assembly Bill 1807, and the Safe Drinking Water and Toxic Enforcement Act (California Proposition 65). Proposition 65 includes a requirement that a list of chemicals known to the state to cause cancer or reproductive toxicity be published. Listed chemicals cannot be discharged into sources of drinking water, and warnings must be provided before exposing the public to any significant amount of a listed chemical. California has also established a drinking water Notification Level for 1,4-dioxane of 3 μg/L. Table 8-5 provides a list of states that have established drinking water guidelines for 1,4-dioxane, along with the corresponding value.

Environmental Fate and Behavior

1,4-Dioxane that enters the atmosphere is expected to degrade fairly quickly. Photooxidation by atmospheric hydroxyl radicals appears to be the most rapid degradation process for 1,4-dioxane in the atmosphere.[31] Howard[31] reported estimated high and low half-lives for 1,4-dioxane in the atmosphere of 3.4 and 0.34 days, respectively.

No adsorption or volatilization data are available for 1,4-dioxane in soil. However, based on this compound's infinite solubility and low estimated log soil-adsorption coefficient of 1.23 (compounds with a log soil-adsorption coefficient of this magnitude are mobile in soil), 1,4-dioxane released to the soil is expected to leach into groundwater. The estimated Henry's law constant suggests that volatilization from moist soils will be slow, but based on its moderate vapor pressure, volatilization from dry soils is possible.[32] 1,4-Dioxane has been

TABLE 8-5 Guidelines and Standards for 1,4-Dioxane

State	Drinking Water Value (μg/L)	Type of Value
California	3	Action Level
Massachusetts	50	Guideline
Florida	5	Guideline
Maine	70	Guideline
Michigan	3	Guideline
North Carolina	7	Guideline
WHO	50	Guideline (proposed)
U.S. EPA	6.1	RBC

Source: Chute and Ginsberg (2005).

found to be resistant to biodegradation and has been classified as relatively nonbiodegradable.[32] Howard [31] reported estimated high and low half-lives for 1,4-dioxane in soil of 6 months and 4 weeks, respectively.

No hydrolysis or volatilization data are available for 1,4-dioxane in surface water.[31] When released to surface water, 1,4-dioxane is not expected to hydrolyze significantly because ethers are generally resistant to hydrolysis.[32] The low estimated Henry's law constant (4.88×10^{-6} atm-m^3/mole) for 1,4-dioxane and its miscibility in water suggest that volatilization will be slow.[32] From its estimated log soil-adsorption coefficient of 1.23, 1,4-dioxane is not expected to significantly absorb to suspended sediments. The Japanese Ministry of International Trade and Industry test confirms that 1,4-dioxane either is not degraded or is degraded slowly.[31] It is expected, therefore, that 1,4-dioxane will not biodegrade extensively in the aquatic environment.

The mobility of 1,4-dioxane in groundwater is directly related to its solubility because very hydrophilic compounds are only weakly retarded by sorption to the aquifer matrix during groundwater transport. Additionally, 1,4-dioxane is not expected to volatilize into the soil above the aquifer, and it does not readily biodegrade. Howard[31] reported estimated high and low half-lives for 1,4-dioxane in groundwater of 12 months and 8 weeks, respectively.

Examples of 1,4-dioxane's behavior in groundwater have been documented at two sites contaminated by chlorinated solvents, the Seymour Superfund Site in Seymour, Indiana and the Gloucester Landfill site near Ottawa, Canada. Retardation factors of 1.0 and 1.1 (average) were estimated for 1,4-dioxane at the Seymour Superfund Site and Gloucester Landfill site, respectively[33,34] A retardation factor of 1.0 indicates that the compound is traveling at or near the groundwater velocity. At both sites, the 1,4-dioxane migrated farther than the plumes of other compounds detected: benzene, chloroethane, and tetrahydrofuran at the Seymour Site; and benzene, 1,2-dichloroethene, 1,2-dichloroethane, and diethyl ether at the Gloucester Landfill.[33,34] The other compounds, except tetrahydrofuran, detected at these sites generally had higher retardation factors than 1,4-dioxane and were more amenable to biodegradation.

1,4-Dioxane has low acute toxicity. The liquid is painful and irritating to the eyes, is irritating to the skin upon prolonged or repeated contact, and can be absorbed through the skin in toxic amounts.[21] Breathing 1,4-dioxane for short periods of time causes irritation to the eyes, nose, and throat in humans. Exposure to large amounts of

1,4-dioxane can cause kidney and liver damage.[21] Acute inhalation exposure of high levels of 1,4-dioxane has caused impaired neurological function and irritation of the eyes, nose, throat, and lungs in humans. These acute effects are not likely to occur at concentrations of 1,4-dioxane that are normally found in the U.S. environment.

The U.S. EPA has not established a reference concentration for chronic inhalation exposure or a reference dose for chronic oral exposure for 1,4-dioxane. No evidence of adverse effects attributable to 1,4-dioxane exposure was found in three epidemiological studies on workers.[21] Dose-related liver and kidney damage has been observed in several species of animals chronically (long-term) exposed by oral, inhalation, and dermal routes.[21]

No information is available on the reproductive and developmental effects of 1,4-dioxane in humans.[35] No evidence of gross, skeletal, or visceral malformations was found in offspring of rats exposed through gavage (experimentally placing the chemical in the stomach).[35] Embryotoxicity was observed only at the highest dose.

Human carcinogenicity data for 1,4-dioxane are inadequate. In three epidemiological studies on workers exposed to 1,4-dioxane, the observed number of cancer cases did not differ from the expected cancer deaths.[21] The U.S. EPA has classified 1,4-dioxane as a Group B2, probable human carcinogen of low carcinogenic hazard. The basis for the Group B2 classification is induction of nasal cavity and liver carcinomas in multiple strains of rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs.[21] The cancer oral slope factor is estimated to be 1.1×10^{-2} milligrams per kilogram per day (mg/kg/day) for 1,4-dioxane.[30] The U.S. EPA calculated a drinking water unit risk of 3.1×10^{-7} μg/L.[30] The U.S. EPA estimates that if an individual was to drink water containing 1,4-dioxane at 3.0 μg/L over his or her entire lifetime, that person would theoretically have not more than a one-in-a-million increased chance of developing cancer as a direct result of drinking water containing this chemical.[35] The U.S. EPA estimates drinking water concentrations providing cancer risks of 10^{-4} and 10^{-5} to be 300 and 30 μg/L, respectively.[30]

1,4-Dioxane has low toxicity to aquatic organisms; toxicity values are greater than 100 mg/L. 1,4-Dioxane is not likely to be acutely toxic to aquatic or terrestrial animals at levels found in the environment.[21]

Treatment Options

1,4-Dioxane is one of the most recalcitrant toxic contaminants in subsurface environments. This compound's persistence and mobility present a challenge to site remediation. All current methods rely on pump-and-treat methods to remove the compound from the aquifer for treatment aboveground. Treatment technologies such as air stripping and carbon absorption are not viable for 1,4-dioxane. 1,4-Dioxane is not amenable to removal by air stripping because of its hydrophilic nature and low volatility. GAC has a very limited capacity for 1,4-dioxane. McGuire et al.[36] observed a 67-percent removal of 1,4-dioxane by GAC treatment. Johns et al.[37] noted that GAC manufactured from pecan and walnut shells removed equal or higher amounts of the compound than conventional GAC (manufactured from coal, coconuts, etc.), but the removal efficiency was only slightly higher than 50 percent. GAC adsorption is not a cost-effective treatment option because GAC has a low absorption capacity for 1,4-dioxane (0.5 to 1.0 milligrams of 1,4-dioxane per gram of GAC at 500 μg/L).[38]

Advanced Oxidation

Pumping and treating 1,4-dioxane with UV/peroxide is the state-of-the-art technology for the remediation of 1,4-dioxane in groundwater. While hydrogen peroxide alone is a strong oxidizing agent, its effectiveness increases dramatically when stimulated by UV light. UV/Fenton and UV/visible/peroxide treatments can also be used to treat 1,4-dioxane but they are typically not cost-effective except in high concentrations (Calgon Carbon Corporation, 1996). UV/Fenton, which is a patented process of Calgon Carbon Oxidation Technologies, involves the addition of a small amount of ferrous iron-based ENOX 510 catalyst (10 mg/L) to the water, pH adjustment between 2 and 4, followed by treatment with UV light.[39] The UV/visible/peroxide treatment is used when the contaminated water has a chemical oxygen demand of approximately 1,000 mg/L.[39] This process uses a patented photocatalyst (ENOX 910) that strongly absorbs both UV and visible light with wavelengths between 20 and 500 nanometers (nm), which significantly increases the lamp energy available to generate hydroxyl radicals.

The two primary design variables that must be optimized in the design of a UV/peroxide system are the UV dose (the total lamp electrical energy in kWh applied to 1,000 gallons of water [kWh per 1,000 gallons]) and the concentration of hydrogen peroxide.[39] According to Calgon Carbon Corporation's (Calgon's) AOT Handbook,[39] the electrical energy per order values for UV/peroxide treatment of 1,4-dioxane typically range between 2 and 6 kWh per1,000 gallons per order.[39] The electrical energy per order is the number of kilowatt-hours of electricity required to reduce the concentration of a contaminant in 1,000 gallons by one order of magnitude (90 percent). The UV/oxidation treatment rate is affected by the initial concentration of 1,4-dioxane. Compounds like 1,4-dioxane with several carbon atoms show a significant relationship between initial concentration and treatment performance. For example, treatment of 100 mg/L of 1,4-dioxane with 200 mg/L hydrogen peroxide requires an electrical energy per order of 11.6, whereas treatment of 200 mg/L of 1,4-dioxane with 500 mg/L of hydrogen peroxide requires an electrical energy per order of 17.9, which indicates a lower treatment efficiency.[39]

Calgon has installed UV/oxidation treatment systems at ten sites where 1,4-dioxane is the main contaminant.[16] Concentrations of 1,4-dioxane being treated by UV/oxidation ranged from 20 to 103,000 μg/L. Capital costs for a UV/peroxide treatment unit range from 80, 000 to 500,000 with operations and maintenance costs ranging from 0.20 to 1.50 per 1,000 gallons.[16] At a chemical manufacturer site in North Carolina, concentrations of 1 to 2.5 mg/L 1,4-dioxane are being treated with UV/oxidation.[40] The treatment system consists of a 3- by 90-kW Rayox reactor system designed to treat up to 615 gpm from influent concentrations up to 2.5 mg/L to <10 μg/L (99.96 percent destruction). Operations and maintenance costs for this system are $ 0.76 per 1,000 gallons.

Biodegradation

Although 1,4-dioxane is considered recalcitrant, its biodegradation has been reported under certain conditions, particularly in cultures capable of degrading tetrahydrofuran and morpholine.[41] Research by Sock [42] using activated sludge from a number of wastewater treatment plants receiving 1,4-dioxane was conducted in two different types of bioreactors. One bioreactor employed a suspended growth culture that was operated as a sequencing batch reactor, and the other bioreactor employed a submerged attached growth culture that was operated in a continuous manner. The bioreactors received a complex feed of biogenic organic compounds, 1,4-dioxane, and tetrahydrofuran. The concentrations of the biogenic organic compounds, 1,4-dioxane, and tetrahydrofuran were varied over time, and eventually the organic compounds and tetrahydrofuran additions were eliminated. In the attached growth bioreactor, complete degradation of 10 mg/L each of 1,4-dioxane and tetrahydrofuran to <1 mg/L (the detection limit) was achieved in the suspended growth bioreactor in 4 weeks.[41] By the seventh week, the concentrations of 1,4-dioxane and tetrahydrofuran were increased to 80 mg/L, and complete degradation was achieved by week 10. The suspended growth bioreactor required a longer time for development of the community, perhaps because microbial retention was less effective.[41] When the feed concentration was 80 mg/L in the suspended growth reactor, 20 weeks were required before complete degradation of both compounds was achieved.[41] After the complex biogenic feed and tetrahydrofuran additions were discontinued in week 29, the attached growth bioreactor operated alone on 1,4-dioxane for 5 weeks, but significant discharge of 1,4-dioxane occurred.[41]

In addition to the results of the attached growth bioreactor summarized above, the results of additional suspended growth bioreactors seeded from the attached growth continuous bioreactor, which consistently removed 1,4-dioxane without having other carbon or energy sources, showed that 1,4-dioxane can serve as a sole carbon and energy source for microbial growth[41]. This conclusion was confirmed by kinetic experiments based on microbial growth. The kinetic experiments indicated that the growth rate of the culture on 1,4-dioxane was relatively slow and appeared to be sensitive to temperature. The growth rate of the culture on 1,4-dioxane was highest at a temperature of 35°C.[41] The culture degrading 1,4-dioxane was a complex bacterial community with several genera present. Researchers were unable to isolate a pure culture capable of growth on 1,4-dioxane alone and were not able to reconstruct the mixed culture from isolated organisms.[43]

The kinetic results suggested that the failure of conventional wastewater treatment plants to remove 1,4-dioxane from wastewater is kinetically based and not based on the bacteria's inability to degrade 1,4-dioxane or on any inhibitory toxic characteristics.[41] A single completely mixed bioreactor is not a feasible configuration for 1,4-dioxane treatment to meet discharge standards because the solids retention time of less than 20 days, typical for these systems, is not long enough to maintain a culture capable of biodegrading 1,4-dioxane.[41] And, the temperature of most activated sludge systems drops below 20°C during winter; at that temperature, the minimum solids retention time would be longer.

Theoretical modeling studies were conducted using the known kinetics of biodegradation to investigate two potential alternative configurations: the use of completely mixed tanks in series as the bioreactor configuration, and the use of pretreatment of segregated 1,4-dioxane-containing streams).[41] The results indicated that using a bioreactor configuration of two or more tanks in series with bioreactor temperatures of 35°C should be used for optimal removal of 1,4-dioxane and that benefits would accrue from longer retention times (more than 9 days).[41] Although it would be impossible to segregate all of the 1,4-dioxane-containing wastewater streams, pretreatment of 1,4-dioxane would reduce the mass flow rate into the activated sludge system of the main bioreactor. The study indicated that this would have a large benefit if the activated sludge system was configured in a tank-in-series arrangement; however, it would not have much beneficial effect on the activated sludge if it contained only a single completely mixed bioreactor.[41] The simplest form of pretreatment would be to use a simple continuous stirred tank reactor with all biomass growth being discharged from it to the activated sludge.[41] Under that condition, the activated sludge system becomes a bioreactor that receives in the influent significant quantities of biomass capable of degrading a slowly degradable compound. The magnitude of the benefit to such a bioreactor depends on the mass input rate of capable biomass relative to the mass rate of capable biomass growth on the specific substrate actually applied to it.[41]

An activated sludge system for treatment of the main wastewater flow and the pretreated esterification wastewater was configured as three tanks-in-series with 50 percent of the system volume in tank 1, and 25 percent each in tanks 2 and 3.[44] These would be operated at ambient temperature because of the high flow rates. CH2M Hill[44] tested the proposed flow scheme, as well as several other schemes at pilot-scale at a fiber manufacturing facility. The system routinely reduced the 1,4-dioxane effluent concentration to less than 40 μg/L, although the influent concentration was not stated.

This study indicates that 1,4-dioxane can be biodegraded in properly configured treatment systems using biological processes. Laboratory-scale studies using the kinetics of 1,4-dioxane must be conducted to determine the optimal configuration of the treatment system followed by pilot-scale tests on wastewater or groundwater influent to scale-up the proposed system.

Research conducted at North Carolina State University by Zenker[45] investigated the ability of subsurface microorganisms from contaminated soil to intrinsically biodegrade 1,4-dioxane in microcosm assays designed to simulate aquifer conditions. Sediment from six locations contaminated with 1,4-dioxane was used to construct sets of microcosms—four were incubated aerobically and two under anaerobic conditions.[45] Each set contained five treatments that broadly examined the effects of 1,4-dioxane concentration, temperature, presence of tetrahydrofuran (a cosubstrate), and nutrient availability on biodegradation. Treatments were incubated for approximately one year, during which time each was sampled periodically for 1,4-dioxane concentration. With the exception of one treatment at one site, no detected biodegradation of 1,4-dioxane occurred in any microcosms.[45] In the one microcosm, complete biodegradation of 1,4-dioxane was demonstrated within 100 to 300 days under enhanced conditions using soil with previous exposure to 1,4-dioxane.[46] The enhanced conditions included the addition of tetrahydrofuran, incubation at 35°C, and the addition of nitrogen, phosphorous, and trace minerals. A subsequent readdition of 1,4-dioxane did not yield further biodegradation until tetrahydrofuran was added. Microcosms incubated under ambient groundwater conditions (16°C) exhibited no biodegradation of 1,4-dioxane.[46] The sediments studied did not demonstrate that intrinsic biodegradation of 1,4-dioxane is occurring. However, 1,4-dioxane degradation by soil microorganisms may be possible under certain conditions.

As part of Zenker's [45] research, a mixed-culture from a 1,4-dioxane-contaminated aquifer with the ability to aerobically biodegrade 1,4-dioxane was enhanced by the presence of tetrahydrofuran. No biodegradation of 1,4-dioxane was observed in the absence of tetrahydrofuran, and the measured cell yield was similar during degradation of 1,4-dioxane with tetrahydrofuran or with tetrahydrofuran alone. However, when the consortium was grown in the presence of [^{14}C]1,4-dioxane and tetrahydrofuran, 2.1 percent of the radiolabeled 1,4-dioxane was present in the particulate fraction. The majority of the ^{14}C (78.1 percent) was recovered as $^{14}CO_2$, while 5.8 percent remained in the liquid fraction.[45]

The biodegradation kinetics of a mixed-culture with the ability to cometabolically degrade 1,4-dioxane in the presence of tetrahydrofuran were also studied using a model capable of incorporating the effects of product toxicity, competitive inhibition, depletion of cellular energy, and enhancement of non-growth substrate biodegradation in the presence of growth substrate.[45] Unlike cometabolism of other chemicals, there was no evidence that the biodegradation of 1,4-dioxane produces toxic by-products. The presence of 1,4-dioxane did not inhibit the biodegradation of tetrahydrofuran, but tetrahydrofuran may inhibit 1,4-dioxane biodegradation.[45] The model adequately simulated biodegradation of 1,4-dioxane and tetrahydrofuran at molar concentrations between 0.9 and 3.3 (mole 1,4-dioxane per mole tetrahydrofuran).

The ability of both a laboratory-scale trickling filter and a rotating biological contractor to biodegrade 1,4-dioxane was also investigated by Zenker.[45] Both reactors received a feed solution designed to mimic 1,4-dioxane concentrations typically encountered in contaminated groundwater. The feed solution contained tetrahydrofuran and 1,4-dioxane. The reactors were operated for approximately one year and were capable of biodegrading 1,4-dioxane at 0.2 to 25 mg/L in the obligate presence of tetrahydrofuran as the growth substrate.[45] 1,4-Dioxane removal rates ranging from 95 to 98 percent were measured in the trickling filter. A simple tank-in-series hydraulic model combined with a kinetic model that incorporated cometabolism was utilized to model the effluent concentration of tetrahydrofuran and 1,4-dioxane from the trickling filter. Model predictions for tetrahydrofuran removal were satisfactory for all loading rates analyzed. However, the model generally overpredicted 1,4-dioxane removal.[45] This research demonstrated the ability to treat low concentrations of 1,4-dioxane through a cometabolic process in attached growth reactors.

Phytoremediation

Although 1,4-dioxane's half-life in soils and groundwater is in the order of years, its half-life in the atmosphere in the presence of nitric oxide and hydroxyl radicals is only 6.7 to 9.6 hours.[47] Researchers hypothesized that if 1,4-dioxane could be volatized from the soil and groundwater to the atmosphere by vegetation with a large leaf index and transpiration rate, then 1,4-dioxane could be remediated.[47] In the atmosphere, the 1,4-dioxane would be rapidly photodegraded. Using this premise, research was conducted at the University of Iowa to assess the viability of using phytoremediation to remediate 1,4-dioxane in groundwater and soils.

The results of the research conducted by the University of Iowa suggest that phytoremediation of 1,4-dioxane may be a viable cleanup alternative. Plants can enhance the removal of xenobiotics by at least two mechanisms: (1) direct uptake and, in some cases, in-plant transformations to less toxic metabolites; and (2) stimulation of microbial activity and biochemical transformations in the rhizosphere (root zone) through the release of exudates and enzymes.[48] Although the latter mechanism is not very effective for removing recalcitrant xenobiotics like 1,4-dioxane, experiments indicate that this mechanism could be enhanced by inoculation of poplar tree roots with actinomycete strain CB1190.[48]

Hydroponic studies were conducted to assess the capacity of hybrid poplar trees for uptake and translocation of ^{14}C-labeled 1,4-dioxane.[48] In the hydroponic studies, hybrid poplar cuttings removed 1,4-dioxane rapidly from a solution containing 23 mg/L 1,4-dioxane. Within 8 days, between 30 and 79 percent removal of the 1,4-dioxane was achieved, with an average removal of 54 percent. Poplars removed 1,4-dioxane more slowly from spiked soil containing 10 mg of 1,4-dioxane per kilogram of dry soil, with 24 percent removal within 18 days. In both experiments, the primary pathway was uptake by transpiration and volatilization from leaf surfaces.[48]

Soil microcosm experiments were also conducted to study the potential to enhance 1,4-dioxane biodegradation in the rhizosphere through bioaugmentation with an actinomycete (strain CB1190). The CB1190 used in the microcosm experiments was grown on a medium of 1,000 mg/L tetrahydrofuran, a similar ether that is preferred by CD1190.[48] CB1190 degraded 100 mg/L 1,4-dioxane in incubations without soil within 1 month. Poplar root extract (ground roots) stimulated 1,4-dioxane microbial degradation in soil of unknown previous exposure to 1,4-dioxane with 100 percent removal within 45 days. 1,4-Dioxane was not removed in sterile controls or in viable microcosms not amended with CB1190 within 100 days. However, some 1,4-dioxane removal occurred after 120 days, indicating that the indigenous soil population may have adapted and developed 1,4-dioxane-degrading abilities. All microcosms amended with CB1190 degraded 1,4-dioxane faster, suggesting the feasibility of bioaugmentation to degrade this compound.[48] Finally, it has been shown that hybrid poplar trees can remove over 80 percent of 1,4-dioxane from soil in 15 days, 76 to 83 percent of which is transpired from leaf surfaces.[49]

Additional bioaugmentation experiments using the 1,4-dioxane-degrading actinomycete, strain CB1190 were conducted at the University of Iowa.[50] The objectives of this research were to determine if poplar trees could enhance the removal and mineralization of 1,4-dioxane from contaminated soil and determine if bioaugmentation with CB1190 could enhance the cleanup process in both planted and unplanted soil.[50] Reactors planted with hybrid poplar trees removed more 1,4-dioxane within 26 days than in unplanted reactors, regardless of whether CB1190 was added. Bioaugmentation with CB1190 enhanced the mineralization of 1,4-dioxane in all experiments. CB1190 increased the percentage of 1,4-dioxane mineralized in unplanted soil from 9 to 26 percent.[50] Experiments were also conducted with excised tree reactors that offer a root zone but do not remove 1,4-dioxane through plant evapotranspiration. More 1,4-dioxane was mineralized in the excised tree reactor with CB1190 (35 percent) than in one without CB1190 (17 percent)[50]. Although CB1190 also enhanced 1,4-dioxane mineralization in planted soil, this enhancement was not statistically significant because plant uptake reduces the availability of 1,4-dioxane for microbial mineralization.[50]

The research summarized above indicates that phytoremediation of 1,4-dioxane in groundwater and soil is a technology that should be studied further. More research into the final metabolites and end-products will be necessary to fully assess the effects of full-scale phytoremediation.[48]

PERCHLORATE

Background and History

During the last decade, perchlorate has been identified as a contaminant of concern for investigations dealing with soil and groundwater contamination. Present in a variety of commercial formulations, perchlorate was brought to the forefront with the development of a low-level laboratory detection method in 1997. Since that time, a variety of sites have been identified as being contaminated with perchlorate, resulting in the need to respond to mitigate the effects on human health and the environment. According to the U.S. EPA, there are ninety-five sites in the United States that have been identified as having a release or a potential release of perchlorate. Perchlorate releases to the environment have been found in 25 of the 50 states. More states are likely to be identified as having releases of perchlorate as analysis of the compound becomes more routine in water systems.

History and Use of Perchlorate

Perchlorate salts are utilized in a variety of applications: solid rocket propellants, electronic tubes, additives to lubricating oils, tanning and finishing leather, aluminum refining, rubber manufacturing, and the production of paints and enamels. Ammonium perchlorate, however, has been the focus of increased scrutiny because of documented groundwater contamination associated with the handling of this material. The

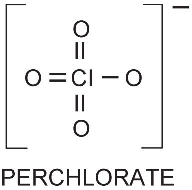


FIGURE 8-3. Perchlorate.

compound is used as an oxidant in the propellant for rockets, missiles, and fireworks. Additionally, ammonium perchlorate is being utilized as a component of airbag inflators. Early data suggested that ammonium perchlorate may also be associated with fertilizer, but subsequent studies found that perchlorate could be found only in fertilizer imported from Chile. Chilean fertilizer represents less that 0.1 percent of the fertilizers used in the United States. The supplier of Chilean nitrate has since taken steps to eliminate or reduce perchlorate levels in their products, the concentration of perchlorate in Chilean fertilizer prior to 2001 may have been high enough to cause comparable contribution to the food chain as that of perchlorate oxidizers.[51]

In 2005, researchers at Texas Tech University demonstrated that perchlorate could be generated naturally in the atmosphere or by surface oxidation. The researchers went on to further demonstrate that these sources might also be a significant contributor to low-level perchlorate contamination in areas that did not have perchlorate manufacturing or munitions activities.

As a solid, ammonium perchlorate is highly reactive and is used as an oxidizer for solid rocket fuel. Ammonium perchlorate is the oxidizer component in a solid composite propellant that includes a binder, aluminum powder, a plasticizer, a ballistic modifier, a bonding agent, and an antioxidant. The solid propellant has a limited shelf life and, as such, requires periodic replacement with fresh material and disposal of the aged material. In the United States, large-scale production of perchlorate compounds began in the mid-1940s. Starting in the 1950s, large quantities of this material had been replaced and disposed of in landfills.

The aged propellant had been land disposed, as well as disposed of by open pit burns and detonation. The waste material and noncombusted propellant has infiltrated into the soil and groundwater, resulting in contamination of both media.[52]

Forty-four states have confirmed the presence of perchlorate manufacturers or users. Based on usage, additional locations may be confirmed as systematic sampling and monitoring programs are instituted at other sites across the country. Based on available information, locations where perchlorate has been manufactured or used are likely candidates for historical releases.

Perchlorate Characteristics

Perchlorate is an anion generated by the dissolution of ammonium, potassium, magnesium, or sodium salts. Table 8-6 provides a summary

TABLE 8-6 Physical and Chemical Properties of the Perchlorate Anion and Perchlorate Salts

	Perchlorate	Ammonium Perchlorate	Potassium Perchlorate	Magnesium Perchlorate	Sodium Perchlorate
CAS Number	14797-73-0	7790-98-9	7778-74-7	10034-81-8	7601-89-0
Molecular formula	ClO_4	NH_4ClO_4	$KClO_4$	$Mg(ClO_4)_2$	$NaClO_4$
Boiling point (°C)	—	—	400[a]	—	—
Melting point (°C)	—	439[b]	525[d]	250[d]	480[e]
Molecular weight (g/mol)	99.45[a]	117.49[b]	138.55[a]	223.20[d]	122.4[a]
Water solubility	—	200 g/L @ 25°C[c]	15 g/L @ 25°C[c]	99 g/1,000-g @ 25°C[e]	209 g/100-g @ 25°C[f]

[a] Budavari, 1996 (as cited in HSDB, 2004).
[b] HSDB, 2004.
[c] Ashford, 1994 (as cited in HSDB, 2004).
[d] Lide, 2000 (as cited in HSDB, 2004).
[e] Weast, 1979 (as cited in HSDB, 2004).
[f] Gerhartz, 1985 (as cited in HSDB, 2004).

of some of the basic physical and chemical properties of the anion and their roles in the behavior of perchlorate in the environment.

The solubility of ammonium perchlorate is reported to be 20.2 g/100 g of solution at 25°C. This value indicates that ammonium perchlorate will readily dissolve and that the perchlorate anion will remain in solution. Ammonium perchlorate is stable when dissolved in water at concentrations as high as 1,000 mg/L.

The oxidation/reduction potential of a compound is represented by the standard potential value. This value suggests that reduction of the perchlorate anion is thermodynamically favorable; however, available studies do not suggest that this reduction occurs spontaneously. The standard potential also indicates that anaerobic and anoxic conditions will promote reduction of the perchlorate anion.

The available literature does not provide a vapor pressure for ammonium perchlorate; however, looking at a similar compound—ammonium chloride—suggests that ammonium perchlorate will not be volatile at ambient temperatures. The density of an ammonium perchlorate solution is greater than the density of water at similar temperatures, which indicates that a concentrated solution of ammonium perchlorate is expected to be denser than water.

Although analytical procedures have existed for some time to detect perchlorate, the methodologies were not suitable for detection at low levels. Prior to 1997, colorimetric and ion chromatographic procedures had been used to detect the presence of perchlorate, and in the case of ion chromatographic procedures, quantitatively measure concentrations in excess of 400 μg/L. Further refinements dropped the detection limit to 100 μg/L, but toxicological issues suggested a detection level at 4 μg/L would be necessary. In March 1997, the California Sanitation and Radiation Laboratory Branch, in conjunction with an analytical equipment manufacturer, developed an ion chromatographic method that had a method detection limit of approximately 1 μg/L and a reporting limit of 4 μg/L. Further refinements in analytical methodologies have incorporated liquid chromatography/liquid chromatography mass spectroscopy techniques to provide greater reliability and better detection limits. The challenge in analyzing for perchlorate has been interference by the sample matrix. Perchlorate analysis in groundwater samples can be affected by other salts, such as nitrate, chlorate, and chloride, although most laboratories are equipped to accommodate these samples. The real challenge has been analyzing perchlorate in fertilizer, food crops, and soil. Obviously, there are significant matrix interference issues with these types of samples that make it increasingly difficult to get reliable results. It is important to consult the most recent research when choosing the analytical methodology for perchlorate.

Regulatory Framework

Perchlorate is not presently regulated by the U.S. EPA. The 1996 Safe Drinking Water Act mandated the U.S. EPA to identify a list of contaminants to be examined for development of regulatory controls if appropriate. The Office of Water placed perchlorate on the Contaminant Candidate List in March 1998, indicating that additional research and information would be required before regulatory determinations could be made. Perchlorate has remained on the Contaminant Candidate List since that time.

Federal regulation of perchlorate really began in 1992 when the U.S. EPA's Office of Research and Development published a provisional reference dose for perchlorate of 0.0001 mg/kg/day based on the effects of potassium perchlorate in patients with Grave's disease (an autoimmune disease that affects the thyroid). In 1995, the Office of Research and Development replaced the reference dose of 0.0001 mg/kg/day with a range estimate of 0.0001 to 0.0005 mg/kg/day. Using some simplifying assumptions of an average body weight of 70 kg and a tap water consumption rate of 2 liters per day over a standard lifetime, an acceptable range of 4 to 18 μg/L of perchlorate in drinking water was derived. The U.S. EPA also released a report in 1999 titled "Toxicological Review and Risk Characterization, Based on Emerging

Information," that included a perchlorate action level of 32 μg/L based on a reference dose of 0.0009 mg/kg/day. The Office of Research and Development released the 1999 interim guidance recommending that risk assessors use the existing reference dose range of 0.0001 to 0.0005 mg/kg/day and recommending maintaining the resulting provisional cleanup levels or action levels of 4 to 18 μg/L.

In an attempt to reconcile the confusion over the science associated with perchlorate toxicity, the National Academy of Sciences was asked to evaluate the existing scientific data and make recommendations as to the reference dose and overall regulation of perchlorate. The National Academy of Sciences published their report in January 2005. The report recommended a reference dose of 0.0007 mg/kg/day. The U.S. EPA adopted a reference dose of 0.0007 mg/kg/day in 2005. According to the National Academy of Sciences report, this reference dose equates to an action level in drinking water of approximately 20 μg/L, which would be protective for pregnant women, fetuses, and newborns.

In 2005, the U.S. EPA issued a recommended Drinking Water Equivalent Level for perchlorate of 24.5 μg/L. In early 2006, the U.S. EPA issued a "Cleanup Guidance" for this same amount. Both the Drinking Water Equivalent Level and the Cleanup Guidance were based on a thorough review of the existing research by the National Academy of Sciences.

The states have taken the lead in developing regulatory standards for perchlorate in the absence of federal regulation. As of June 2004, eight states have adopted guidance levels and/or action levels for perchlorate[53] These levels are presented in Table 8-7. States are faced

TABLE 8-7 Perchlorate Regulatory Status

State	Guidance Level (μg/L)	Action Level (μg/L)
California[a]	6	6
New York	5[b]	18
Texas[c]	Not applicable	4
Arizona	14	Not applicable
Massachusetts	1	Not applicable
Maryland	1	Not applicable
New Mexico	1[d]	Not applicable
Nevada	Not applicable	18

[a] California: On March 12, 2004 California OEHHA published a Final Public Health Goal = 6 μg/L and the CDHS Drinking Water Program revised its perchlorate action level upward from 4 to 6 μg/L.
[b] New York: "Drinking Water Planning Level."
[c] Texas: Residential Groundwater Cleanup Level 4 μg/L; Industrial/Commercial Groundwater Cleanup Level 7–10 μg/L (depends on whether the site falls under the old or new Risk Reduction Program).
[d] New Mexico: "Interim Groundwater Screening Level."

with a dilemma in regulating perchlorate ahead of a published federal standard. If states promulgate a level that ultimately ends up being higher than a future federal level, then there is the potential for significant increased costs in monitoring and cleanup by parties that had initially responded to a state's level. As a result, states have been eagerly awaiting the publication of guidance from the U.S. EPA. The National Academy of Sciences report was supposed to remove any uncertainty associated with setting a federal standard; however, the report itself has been called into question, and the recommended reference dose in the report has been questioned. Because the U.S. EPA has decided not to set a regulatory standard for perchlorate, the states have been put in the position of developing regulatory guidance that satisfies their citizens. On August 1, 2006, Massachusetts became the first state to set a drinking water standard for perchlorate at 2 μg/L. California proposed an MCL of 6 μg/L on August 7, 2006, and it became official on October 18, 2007.

Environmental Fate and Behavior

Behavior of the perchlorate anion is controlled by its basic chemical properties. As an oxidant, the reduction of the chlorine atom occurs slowly. Retardation to soil is not expected to be significant because perchlorate has a low affinity for the organic content in soil. As discussed, the compound is very soluble in water and does not interact with the organic content of the soil matrix in the aquifer. The half-life of perchlorate in a typical groundwater environment seems to be very long. Therefore, perchlorate travels close to the velocity of groundwater, and the resulting plumes can be very large.

In 1985 using colorimetric procedures, region IX of the U.S. EPA encountered perchlorate concentrations ranging from 0.11 to 2.6 mg/L in 14 drinking water wells. The Centers for Disease Control was contacted to offer assistance relative to the potential health effects of perchlorate at these concentrations. The Centers for Disease Control's recommendation was to validate the colorimetric results, but they were unable to assist with the potential toxicity issues because of lack of data. The U.S. EPA region IX focused on other chemicals at these wells because a suitable analytical procedure and relevant toxicity data were unavailable.

The U.S. EPA region IX, however, encountered perchlorate concentrations again at a California Superfund site in excess of 1 mg/L in monitoring wells. Consequently, efforts were intensified to establish a human health-based reference dose. A request to the U.S. EPA

Superfund Technical Support Center resulted in the release of provisional reference dose values in 1992, which were then revised in 1995. Groundwater cleanup guidance levels ranging from 4 to 18 μg/L were calculated based on existing information and utilizing standard assumptions relative to exposure pathways, ingestion, and body weight.

After development of a suitable analytical method for low-level detection of perchlorate in 1997, the existing toxicological database was consulted to determine the adequacy of the existing information relative to perchlorate. At that time, the existing data were found to be inadequate for the purposes of performing quantitative exposure assessments for humans. Since that time, a number of studies have been performed, and the database has increased, but additional data are still needed and are being gathered.

The principal exposure route for perchlorate is through oral uptake. When consumed, perchlorate is readily absorbed from the intestinal tract. Neither dermal exposure nor inhalation is a probable exposure pathway. When in the body, perchlorate competes with iodide in the thyroid, which causes a decrease in thyroid hormone production. The consequence of this behavior raises concerns relative to potential carcinogenic, neurodevelopmental, developmental, reproductive, and immunotoxic effects. Additionally, limited information is available to address potential ecotoxicological effects from perchlorate.

Perchlorate is readily degraded anaerobically by bacteria. Perchlorate acts as an alternate electron acceptor (similar to nitrate) in anaerobic or microaerophilic environments. However, perchlorate does not appear to be degraded in the aerobic environments that are typical of western aquifers. The characteristics of the aquifers in the western United States (i.e., aerobic, low organic content) tend to favor the migration of perchlorate.

Perchlorate is also readily taken up by leafy plants such as lettuce and has been found in crops that were irrigated with water containing perchlorate.[54] As previously mentioned, the analysis of perchlorate in vegetables and other plant materials is very difficult because of matrix interference. Research continues on the overall effect that perchlorate in food crops may have on human health.

Treatment Options

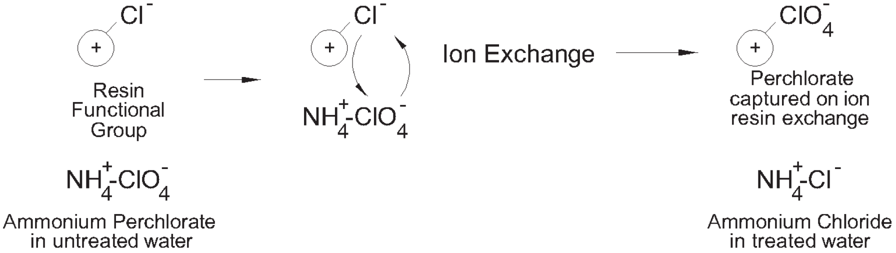
Treatment technologies have been developed to remediate perchlorate-contaminated groundwater. Perchlorate does not naturally attenuate in soils or aquifers, and because the compound is not organic, bacteria will not use it as a food source but will use it as a final electron acceptor. Other in situ methods will not work because of the chemical properties of perchlorate. Because perchlorate is not volatile, it will not partition into an airstream; therefore, air sparging will not treat perchlorate.

Most perchlorate treatment methods are ex situ technologies that require it to be pumped aboveground for treatment. Pump-and-treat systems have been used to capture perchlorate plumes and convey the contaminant to aboveground treatment systems. Conventional filtration and sedimentation processes are not effective perchlorate treatment technologies, and GAC is only slightly effective in removing perchlorate (GAC has limited perchlorate adsorptive capacity). Aboveground treatment technologies are currently being used and are being optimized to provide more cost-effective perchlorate treatment.

Ion Exchange

Ion exchange has a demonstrated history of successfully treating perchlorate and has been implemented at numerous sites throughout the United States for remediation and drinking water treatment. The process involves the substitution of an innocuous anion—generally chloride—for the perchlorate anion. The anion exchange process for perchlorate removal is illustrated in Figure 8-4.

Calgon successfully demonstrated the use of ion exchange to remove perchlorate from groundwater. In a study funded by the Main San Gabriel Watermaster for the Big Dalton well, Calgon conducted a pilot study of their ISEP system in 1998. Calgon's ISEP process is a continuous countercurrent ion exchange system that removes perchlorate



Note: Ammonium perchlorate was used as an example. Other forms of perchlorate, such as sodium perchlorate, may also be treated by ion exchange.

FIGURE 8-4. Anion exchange process for perchlorate removal.

from water. The process uses an ion exchange resin that is continuously regenerated with a sodium chloride brine solution. The system demonstrated effective removal of perchlorate (18 to 76 μg/L) to nondetectable (<4 μg/L) concentrations, as well as removal of nitrate and sulfate from the water. The brine generated from the regeneration of the ion exchange resin has significantly elevated concentrations of perchlorate, nitrate, and sulfate—several orders of magnitude higher than the influent water. However, the brine volume represents only 0.75 percent of the treated influent volume. Although the volume of brine generated by the ISEP system is only a small percentage of the treated influent, it still generates a significant volume of liquid waste that requires disposal; therefore, to improve the cost-effectiveness of the technology, the brine must be further treated to destroy the concentrated perchlorate, nitrate, and sulfate. To reduce the volume of brine that must be disposed of as a liquid waste, Calgon developed an add-on module for the ISEP system that destroys the perchlorate and nitrate and removes the sulfate from the regeneration brine. This perchlorate and nitrate destruction module further reduces the volume of brine that must be disposed of as a liquid waste and requires the disposal of only a small volume of concentrated sulfate solution.

In a separate pilot demonstration, Calgon successfully demonstrated the use of the perchlorate and nitrate destruction module in the overall treatment train. The perchlorate and nitrate destruction module contains a catalytic reactor for perchlorate and nitrate reduction and a nanofiltration unit for sulfate separation. Funded by the National Aeronautics and Space Administration (NASA), groundwater at the Jet Propulsion Laboratory in Pasadena, California, was contaminated with trichloroethene, 1,2-dichloroethane, carbon tetrachloride, and perchlorate (up to 1,200 μg/L). GAC was used to remove the VOCs from the groundwater prior to being treated by the ISEP system. For this pilot test, Calgon constructed a treatment platform that included the ISEP® module and the perchlorate and nitrate destruction module. The resulting platform is referred to as an integrated ISEP+ system. The pilot study demonstrated the successful removal of all the constituents to nondetectable concentrations, as well as the subsequent destruction of perchlorate and nitrate and the removal of sulfate (exceeding 96 percent). After treatment by the perchlorate and nitrate destruction module, the brine was recycled for resin regeneration, and a small volume of sulfate-rich brine was disposed of as a liquid waste.

Although there are a number of ISEP systems operating today, newer ion exchange resins have been developed that have much higher perchlorate capacities than the ion exchange resins that were first used to treat perchlorate. Because of this, Calgon markets their ISEP system only for nitrate treatment applications. These new ion exchange resins have extremely high perchlorate removal capacities (1 gallon of resin can treat 100,000 to 200,000 gallons—or more—of water), but they cannot be regenerated with the standard brine solution, so they are implemented in a two-vessel, lead-lag configuration similar to GAC treatment for VOCs discussed earlier in the book. When the ion exchange resin in the lead bed is saturated with perchlorate (often referred to as "spent resin"), it is removed from the vessel, transported to a solid waste disposal facility, and managed as a solid waste (generally spent resins are incinerated); fresh resin is installed into the lead vessel, the old lag vessel becomes the new lead vessel, and the fresh resin is placed in service as the lag vessel. This nonregenerable ion exchange process is the most widely used technology for perchlorate treatment. To make ion exchange treatment more cost-effective, Oak Ridge National Laboratories (ORNL) developed a regeneration technology that regenerates the newer, high-capacity perchlorate resins with a ferric chloride and hydrochloric acid solution at elevated temperature and pressure.[55,56] The perchlorate in the regeneration solution is then catalytically reduced to chloride ion and water and is then recycled as fresh regenerant.[57] This technology would likely be implemented by transporting spent resins to a regeneration facility instead of a waste management facility, and the regenerated resin would be returned to the treatment facility. ARCADIS, Calgon, and ORNL are currently demonstrating this resin regeneration technology in an Environmental Security Technology Certification Program (ESTCP)-funded project in Fontana, California.

Additional research has been conducted to treat concentrated perchlorate in regeneration brines. These technologies include biological treatment, reverse osmosis, thermal destruction, and electrolytic treatment.[58]

Tailored Granular Activated Carbon

As previously discussed, conventional GAC has a very limited capacity for perchlorate. To increase the perchlorate capacity, researchers at Pennsylvania State University developed a tailored granular activated carbon (TGAC) that has a perchlorate capacity approximately 35 times greater than conventional GAC.[59] An advantage of this technology is that it could simultaneously treat perchlorate- and VOC-contaminated water with one type of medium, which could make it a cost-effective technology for mixed-contaminant plumes.

Pennsylvania State University and U.S. Filter (now Siemens), in conjunction with the City of Redlands, California, conducted a pilot study for drinking water treatment with TGAC. Organic monomers or polymers were used as the tailoring agents and increased the perchlorate capacity of the GAC by making it behave like an ion exchange resin. Laboratory tests conducted on water from the City of Redlands site (60 to 70 μg/L of perchlorate) revealed that the TGAC had a treatment capacity between 30,000 and 35,000 bed volumes (i.e., 1 gallon of TGAC could treat between 30,000 and 35,000 gallons of water) before initial perchlorate breakthrough.[59]

A typical TGAC application would be very similar to GAC treatment for VOCs and ion exchange for perchlorate treatment. When the TGAC reaches perchlorate saturation, it would be removed from the vessel and managed as a solid waste, or it could be reactivated, retailored, and returned to service. This technology is not yet commercially available. ARCADIS, Pennsylvania State University, Siemens, and the Air Force Institute of Technology are currently demonstrating the TGAC technology in an ESTCP-funded project in Fontana, California.

Reverse Osmosis

Preliminary studies indicate that reverse osmosis can remove low concentrations of perchlorate from contaminated water. Reverse osmosis utilizes a fine filter/membrane that contaminated water is forced through. As the water passes through the membrane, perchlorate is removed, and perchlorate-free water exits the filter. Similar to the ion exchange process, concentrated perchlorate-laden brine called "rejectate" is generated that must be properly managed and disposed of as a liquid waste stream.

U.S. Filter (now Siemens) assisted the Jet Propulsion Laboratory in identifying remedial technologies that were capable of treating groundwater contaminated with perchlorate. U.S. Filter identified reverse osmosis as one of the potential remediation technologies. Reverse osmosis was identified as having no chemical requirements except for the chemical usage for controlling scaling. The process has demonstrated success in removing perchlorate and other inorganic constituents from water. Performance results were provided for a thin-film composite membrane and a cellulose acetate membrane. The influent water had a perchlorate concentration of 800 μg/L, and the resulting permeate (treated water) had concentrations of approximately 4 to 18 μg/L for the thin-film composite membrane and approximately 600 μg/L for the cellulose acetate membrane.

Best Technology Company successfully demonstrated reverse osmosis as a viable treatment technology for perchlorate and demonstrated that the reverse osmosis rejectate could subsequently be treated biologically. Reverse osmosis reduced perchlorate concentrations from 35 to <4 μg/L at a flow rate of approximately 4 gpm, and the reverse osmosis rejectate was biologically reduced in an EcoMat Hall bioreactor (described later in this chapter) that reduced perchlorate concentrations from approximately 110 to <4 μg/L at a flow rate of approximately 1 gpm.[60]

Biodegradation

The use of microbes to convert perchlorate to a less toxic or innocuous substance has received considerable attention and success. As discussed earlier, the standard potential of perchlorate suggests that the anion will be reduced in anaerobic conditions. To date, efforts have focused on the development of a suitable biochemical reduction process to promote the anaerobic reduction of perchlorate. In one study, the bacterium perclace was cultivated on acetate in an anaerobic environment and then placed in celite-packed columns for use in a flow-through system. Experimentation showed that the system was capable of reducing perchlorate concentrations from 738 μg/L to below detection limits at a flow rate of 1 milliliter per minute (mL/min). Doubling the flow rate reduced the perchlorate degradation effectiveness of the system to approximately 92 to 95 percent. Further experimentation demonstrated that the use of a circulating pump and multiple passes through the media allowed flow rates to increase to 3 mL/min and still achieve a 95-percent perchlorate removal rate.[61]

Full-scale bioreactor systems developed in the late 1990s demonstrated the ability of this technology to successfully reduce perchlorate concentrations from over 5,000 μg/L to the low hundreds micrograms per liter. Of particular note is pilot-scale test that was performed at the San Gabriel Valley Superfund site in California. A bioreactor system successfully treated groundwater with approximately 150 μg/L of perchlorate to nondetectable concentrations. The expected outcome of this work is to develop a system capable of treating 20,000 gpm. The treated water will be supplied to local drinking water utilities for additional treatment and distribution. Public perception and acceptance, however, may require modifications to this plan. Historically, the public does not accept biological treatment methods for drinking water; however, in April 2002, the California Department of Health Services issued conditional approval for the use of fluidized bed reactors for perchlorate treatment of drinking water if 11 conditions are met. To date, no fluidized bed reactors systems have been implemented to treat drinking water.

A fluidized bed reactor has been successfully used at the Aerojet site (Rancho Cordova, California) as part of the Jet Propulsion Laboratory Remediation Project. U.S. Filter/Envirogen (now Shaw) designed and operated a 4,000-gpm fluidized bed reactor with an influent containing 6 mg/L perchlorate and 1.5 mg/L nitrate for treatment. Effluent concentrations for perchlorate and nitrate were <4 and <0.1 μg/L, respectively.[58]

Other types of bioreactors have also been successful in reducing concentrations of perchlorate. Packed bed reactors have been tested at the Crafton-Redlands Site in Redlands, California; the Naval Weapons Industrial Reserve Plant in McGregor, Texas; and the Jet Propulsion Laboratory site. Another bioreactor that has been shown to degrade perchlorate is the hydrogen-based hollow-fiber membrane biofilm reactor. This reactor design utilizes a composite membrane that supports the growth of the biofilm across the surface. This bioreactor was tested at La Puente, California, and successfully reduced perchlorate from 60 to 3 μg/L.[62] The bioreactor utilized approximately 7,000 fibers with approximately 13 cubic meters (m^3) of biofilm surface area. The major advantage of the membrane biofilm reactor is that it produces less biomass than other bioreactors because it utilizes gaseous hydrogen as the electron donor. The EcoMat Hall bioreactor—mentioned in the reverse osmosis section above—is a hybrid of a continuously stirred tank reactor and a fixed film bioreactor. This design continuously circulates a plastic substrate by induced flow from the water being treated. The reactor successfully reduced perchlorate concentrations in laboratory studies and bench-scale tests using methanol and acetate as the electron donor.[63]

Phytoremediation

Initial studies have shown that trees and plants can also create the environment where perchlorate is degraded. Research using willows and eucalyptus species successfully reduced perchlorate concentrations of 10, 20, and 100 mg/L to below 2 μg/L concentrations.[64] Additionally, spinach, French tarragon, and *Myriophyllum* (an aquatic plant) also removed perchlorate from water. The phytoprocesses identified as instrumental to the remediation of perchlorate contaminated water are (1) uptake and phytodegradation in the plant organs, and (2) rhizodegradation as a result of associated microorganisms. The experimental approach suggests that contaminated groundwater could be remediated by irrigation of the intensively cultivated parcels using the successful species. However, the success of this approach will be limited by the capacity of the soil and the plantings to handle potentially large volumes of water.

In situ Bioremediation

The aboveground use of biodegradation has shown that perchlorate will act as a final electron acceptor under reducing conditions. Several studies have been conducted using the IRZ technology (Chapter 4) to change the environment to reducing conditions in order to degrade perchlorate in situ. IRZ pilot testing was conducted at the Whittaker Ordinance Site in Whittaker, California, from September 2001 to April 2003 to treat perchlorate-contaminated groundwater. This project involved the injection of an electron donor, corn syrup, into the groundwater every 60 days. An anaerobic zone was created within 30 days from the first injection event. Perchlorate was reduced from approximately 275 mg/L to approximately 20 mg/L in approximately 18 months.[65] Other tests were conducted at the Aerojet site where perchlorate-impacted groundwater was pumped to the surface, amended with bacterial cultures (for TCE treatment) and electron donors (i.e., calcium magnesium acetate, sodium acetate, and sodium lactate), and then reinjected back into the aquifer. This test demonstrated that perchlorate could be reduced from 12,000 mg/L to below detection limits within 15 feet of the electron donor injection well.[66] A subsequent 72-day test at the Aerojet site showed that perchlorate could also be reduced in the same manner using ethanol as the electron donor—perchlorate was reduced from 8 mg/L to below detection limits.[66] A similar test is being conducted with a line of injection wells at the same site to act as a permeable biobarrier. More tests have been conducted at numerous other sites across the nation.

Permeable Reactive Barriers

Permeable reactive barriers, as previously discussed in the book, have also been applied to perchlorate-impacted groundwater. These barriers can be installed as either a funnel-and-gate or a trench. For perchlorate treatment applications, the permeable reactive barriers are constructed with electron donors to stimulate reduction of perchlorate and organic substrates to nourish the microorganisms.[66] Two full-scale and one pilot-scale permeable reactive barrier applications have been conducted to treat perchlorate. A full-scale permeable reactive barrier system has been installed at the Naval Weapons Industrial Reserve Plant in McGregor, Texas, to address perchlorate and trichloroethene. This system included seven permeable reactive barriers ranging from

100 to 750 feet in length, for a total length of 3,500 feet. The trenches were installed on 1,000-foot centers and were backfilled with 70 percent gravel, 20 percent mushroom compost, and 10 percent soybean oil-soaked woodchips (approximately 4,200 tons of backfill). These permeable reactive barriers reduced perchlorate concentrations by 99 percent from 13 mg/L to below detection limits, and the treatment envelope reached 400 feet downgradient.[66]

Emerging Technologies

Research is still being conducted on several technologies that may be viable with additional research and development. These include the following:

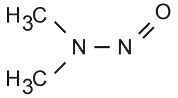
- Nanoscale bimetallic particles
- Titanium^{3+} chemical reduction
- ZVI reduction under UV light
- Capacitive deionization
- Electrodialysis
- Catalytic gas membrane

n-NITROSODIMETHYLAMINE AND OTHER NINTROSAMINES

Background and History

n-Nitrosodimethylamine is a yellow liquid that has no distinct odor and is formed by the nitrosation of dimethylamine with a nitrite ion. Short-term or long-term exposure of animals to water or food containing *n*-nitrosodimethylamine is associated with serious health effects, such as liver disease and death.

n-Nitrosodimethylamine is used primarily in research, but it has had prior use in the production of 1,1-dimethylhydrazine for liquid rocket fuel and in a variety of other industrial uses; e.g., a nematocide, a plasticizer for rubber, in polymers and copolymers,



N-NITROSODIMETHYLAMINE
(NDMA)

FIGURE 8-5. 5 *n*-Nitrosodimethylamine.

a component of batteries, a solvent, an antioxidant, and a lubricant additive. *n*-Nitrosodimethylamine was reported to be present in a variety of foods, beverages, drugs, and in tobacco smoke; it has been detected as an air pollutant, in treated industrial wastewater, treated sewage proximal to a 1,1-dimethylhydrazine manufacturing facility, deionized water, high nitrate well water, and chlorinated drinking water.[67] *n*-Nitrosodimethylamine is unintentionally formed during various manufacturing processes at many industrial sites and in air, water, and soil from reactions involving other chemicals called alkylamines. Alkylamines are both natural and man-made compounds that are found widely distributed throughout the environment.

The most recent data have demonstrated that *n*-nitrosodimethylamine is also a drinking water disinfection by-product that is associated with the use of chloramines. It is expected that more and more water utilities will be using chloramines for disinfection in an attempt to reduce the formation of trihalomethanes and haloacetic acids that are formed when chlorine is used as the primary disinfection agent.

Optimization of drinking water disinfection to minimize the formation of *n*-nitrosodimethylamine is recommended; however, little is known about the mechanism of *n*-nitrosodimethylamine formation in the disinfection process.

n-Nitrosodimethylamine Characteristics

n-Nitrosodimethylamine does not persist in the atmosphere. When n-nitrosodimethylamine is released into the atmosphere, it breaks down in sunlight in a matter of minutes.[68] When released to soil surfaces, *n*-nitrosodimethylamine may evaporate into air, break down upon exposure to sunlight, or sink into deeper soil. The rate of breakdown in water is unknown.

n-Nitrosodimethylamine has a normal boiling point of 154°C and a specific gravity of 1.006, and it is highly soluble in water (100 g/L). The vapor pressure of *n*-nitrosodimethylamine is 3 mmHg, so it can be considered a semi-volatile compound. The Henry's law constant has been estimated at 2.63×10^{-4} atm M^{-1}, indicating that *n*-nitrosodimethylamine is not readily volatilized from water. *n*-Nitrosodimethylamine has a log octanol-water partition coefficient of –0.57, indicating that it is not amenable to activated carbon treatment. The log soil-adsorption coefficient of *n*-nitrosodimethylamine is reported to be 8.5, indicating that it will not have a high affinity for the organic fraction of soil. *n*-Nitrosodimethylamine breaks down rapidly in sunlight (half-life of 5 to 30 minutes) and within a few months in deeper soil (half-life of 50 to 55 days).[69]

Several approaches are available for analysis of *n*-nitrosodimethylamine at levels at or below 2 ng/L (0.002 µg/L). Continuous liquid–liquid extraction or similar techniques capable of reproducible recovery (<20 percent relative standard deviation precision), such as the gas chromatography/mass spectroscopy signal intensity, is sufficient to achieve the concentration at or below 2 ng/L that is required. Gas chromatography/mass spectroscopy methods offer the most sensitive and definitive measurement systems for analysis of *n*-nitrosodimethylamine in the low ng/L range. High-resolution electron impact mass spectrometry and low-resolution chemical ionization (using ammonia, methanol, etc.) or other mass spectrometric techniques with equivalent sensitivity are also acceptable.

Regulatory Framework

Because *n*-nitrosodimethylamine historically has not been considered a common drinking water contaminant, it has no state or federal MCL. In the absence of drinking water standards, California's Department of Health Services uses a drinking water "notification level" (was formerly called an "action level") for the protection of public health.

California's Office of Environmental Health Hazard Assessment lists *n*-nitrosodimethylamine as a chemical known to the State of California to cause cancer (Title 22, California Code of Regulations [22 CCR], Section 12000). The Office of Environmental Health Hazard Assessment's 10^{-5} level corresponds to an exposure of 0.04 micrograms per day [2 CCR Section 12705(b)(1)], which equates to an acceptable drinking water concentration of 0.02 µg/L.

The U.S. EPA classifies *n*-nitrosodimethylamine as a probable human carcinogen based on the induction of tumors at multiple sites in laboratory animals exposed by various routes. The U.S. EPA's 10^{-6} risk level in drinking water corresponds to a concentration of 0.0007 µg/L.[70]

Risk assessments from California's Office of Environmental Health Hazard Assessment and the U.S. EPA identify lifetime *de minimis* (i.e., 10^{-6}) risk levels of cancer from *n*-nitrosodimethylamine exposures as 0.002 and 0.0007 µg/L, respectively. A *de minimis* risk is considered to be below regulatory concept 10^{-6} risk level and corresponds to up to one excess cancer case per million while drinking 2 liters of water per day for a 70-year lifetime.

In April 1998, California's Department of Health Services initially established an action level for *n*-nitrosodimethylamine of 0.02 µg/L.

However, analytical capabilities did not enable detection at that concentration, and detectable quantities of *n*-nitrosodimethylamine exceeded the action level.

In fall 1999, coincidental with more sensitive analytical methods becoming available, the Department of Health Services began working with utilities in the state to investigate the formation of *n*-nitrosodimethylamine during drinking water treatment processes. During this investigation phase, the Department of Health Services established a temporary action level of 0.02 μg/L for *n*-nitrosodimethylamine that became effective in 1999. In November 1999, the Department of Health Services initiated studies with drinking water utilities to investigate the occurrence of *n*-nitrosodimethylamine in raw, treated, and distributed water; the role water quality and treatment processes may play in the formation of *n*-nitrosodimethylamine; and the possible extent of *n*-nitrosodimethylamine formation at various steps in the water disinfection process. These studies found that the formation of nitrosamines in drinking water was considered a by-product of disinfection processes. In 2004, a notification level was set for *n*-nitrosodiethylamine. In 2005, studies found the formation of *n*-nitroso-*n*-propylamine and *n*-nitrosodimethylamine associated with the evaluation of disposable anion exchange resins for drinking water treatment of perchlorate-contaminated waters. As a result, *n*-nitroso-*n*-propylamine was added to the list of chemicals with notification levels in California. As of 2007, the notification levels for these nitrosamines in California drinking water were 10 ng/L for each compound.

Environmental Fate and Behavior

n-Nitrosodimethylamine is highly soluble in water and does not interact with the soil in the aquifer because of its low log soil-adsorption coefficient. As a result, *n*-nitrosodimethylamine will travel close to the velocity of groundwater and does not seem to naturally attenuate in the aquifer. Findings of controlled column experiments suggest that *n*-nitrosodimethylamine and six other *n*-nitrosamines (*n*-nitrosodiethylamine, *n*-nitrosomethylethylamine, *n*-nitroso-*n*-propylamine, *n*-nitrosodi-*n*-butylamine, *n*-nitrosopiperidine, and *n*-nitrosopyrrolidine) are biodegradable under oxic and anoxic redox conditions. Half-lives determined in the study for the targeted compounds varied between 1.3 and 7 days, which the researchers felt would ensure a removal to below detection limits (<2 ng/L) within short travel times in groundwater recharge systems. Findings of the study suggest that complete removal of *N*-nitrosamines requires the presence of an adapted bio-community, which could be established over several weeks to months in groundwater recharge systems.[71]

Treatment

n-Nitrosodimethylamine has a relatively high vapor pressure, high water solubility, and a correspondingly low Henry's law constant. Because of this, air stripping and air sparging are ineffective at treating *n*-nitrosodimethylamine. Reverse osmosis is not effective because *n*-nitrosodimethylamine is a small, uncharged molecule. *n*-Nitrosodimethylamine is hydrophilic and does not sorb well onto GAC or other substrates. It can be adsorbed onto GAC, but vendor literature suggests the removal is highly dependent on the influent concentration, and this method of treatment is practically applied only to concentrations in the 5- to 10-mg/L range. At a concentration of 10 mg/L, a saturated loading rate of 16 percent (16 pounds of *n*-nitrosodimethylamine per 100 pounds of GAC) may be achieved based on vendor isotherm data.[72] At concentrations below 5 mg/L, the saturated loading rate decreases to less than 0.1 percent.[72] Effluent concentrations achievable under these conditions were not provided. Rohm and Haas' Ambersorb 572 adsorptive medium has the highest *n*-nitrosodimethylamine sorption capacity, followed by coconut shell GAC. But, Ambersorb 572 has low Freundlich isotherm K (adsorption capacity) and 1/n (intensity of adsorption) values of 9.65×10^{-3} mg/g and 1.17, respectively, which corresponds with high treatment costs.[73]

Biodegradation

The natural attenuation rate of *n*-nitrosodimethylamine seems to be very slow. One problem may be the extremely low concentrations that require treatment. Biological and abiotic reactions may be limited because of the low concentrations. The natural attenuation that may occurs with *n*-nitrosodimethylamine at microgram per liter concentrations may shut off at nanogram per liter concentrations.

Advanced Oxidation

The most common treatment technology for ex situ *n*-nitrosodimethylamine treatment is photolysis by UV radiation.[73] Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. Light is composed of tiny energy packets called photons, whose energy is inversely proportional to the wavelength of the light. Thus, shorter wavelengths have higher energies. The optimal wavelength for the photooxidation of *n*-nitrosodimethylamine is between 220 and 240 nm.[74] The UV light range is considered to be wavelengths below 400 nm.

As discussed in the 1,4-dioxane section above, electrical energy per order is used to scale-up UV systems from pilot-scale to full-scale. Vendor data show that 90-percent removal of nanogram per liter and microgram per liter concentrations of *n*-nitrosodimethylamine can be achieved at an electrical energy per order (UV dose) of 2.4 kWh per 1,000 gallons per order.[74] This UV dose requires a power consumption of 2.5 kWh per 1,000 gallons, which at a typical rate of \$0.10/kWh results in a reasonable treatment cost of approximately \$0.25 per 1,000 gallons for energy alone. Results from a pilot test conducted by ARCADIS Geraghty & Miller in 1995 on a groundwater containing 230 μg/L *n*-nitrosodimethylamine achieved 99.6-percent destruction of *n*-nitrosodimethylamine using 12 kWh per 1,000 gallons.

As an alternative to UV photolysis systems, sunlight can also be used to photodegrade *n*-nitrosodimethylamine. *n*-Nitrosodimethylamine breaks down in a matter of minutes when exposed to sunlight. In parts of the United States, solar treatment ponds have been used. Successful implementation of such a remedy requires careful evaluation of the amount of sunlight available, precipitation, evaporation, and daily temperatures. This method of treatment has been implemented in California. Other areas of the country where this method may be applicable include Arizona, Nevada, and New Mexico.

Emerging Technologies

The following are a few other *n*-nitrosodimethylamine treatment technologies being researched:

- *ZVI*: ZVI catalyzes *n*-nitrosodimethylamine transformation by hydrogenation, which leads to the formation of dimethylamine and ammonia. But, because of the relatively slow reaction kinetics, this technology may not be cost-effective).[73]
- *Biodegradation*: Laboratory studies have observed *n*-nitrosodimethylamine degradation under both aerobic and anaerobic conditions, and mineralization has also been observed in two studies. There is only limited evidence of *n*-nitrosodimethylamine degradation in the field, and the responsible microorganisms and degradation pathways have not been identified.[73]

- *Phytoremediation*: There is little evidence that *n*-nitrosodimethylamine may be treated by phytoremediation, but because it is highly soluble in water, it may be amenable to transpiration.

ARSENIC

Background and History

Arsenic is included here as an emerging contaminant not because it wasn't previously regulated but because the regulations have changed significantly. On January 22, 2001, the U.S. EPA adopted a new standard for arsenic in drinking water of 10 µg/L—the previous standard was 50 µg/L. The rule became effective on February 22, 2002, and drinking water systems had to comply with the new 10 µg/L standard by January 23, 2006. The current U.S. EPA standard of 10 µg/L is consistent with the World Health Organization's recommended level in drinking water.

The challenge with meeting the new arsenic standard in the United States is that sources of arsenic in water include natural sources such as rock and soil. Elevated concentrations of arsenic are found more frequently in groundwater than in surface water. While the average arsenic concentration measured in groundwater in the United States is less than or equal to 1 µg/L, there are areas in the United States where the naturally occurring concentrations of arsenic exceed 50 µg/L. Most of the systems containing elevated levels of naturally occurring arsenic are found in the western portion of the United States because larger water systems are more likely to obtain their water supplies from a combination of surface water and groundwater, while smaller systems may rely solely on groundwater as a source. Smaller systems are likely to be affected by this change in standard. The U.S. EPA estimated that about 4,000 of the regulated water systems (5.5 percent) were likely to exceed the 10-µg/L standard.

Arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh and neighboring countries.

$$As^{3+}$$

ARSENIC

FIGURE 8-6. Arsenic.

It is estimated that approximately fifty-seven million people are drinking groundwater with arsenic concentrations above the World Health Organization's standard of 10 μg/L. The arsenic in the groundwater is naturally occurring and is released from the sediment into the groundwater because of the anoxic conditions of the subsurface. Many other countries in Southeast Asia, such as Vietnam, Cambodia, and Tibet, are thought to have geological environments similarly conducive to the generation of high arsenic concentrations groundwater.

Arsenic Characteristics

The most common oxidation states for arsenic (As) are $^{-}3$ (arsenides: usually alloy-like intermetallic compounds), $^{+}3$ (As[III] or arsenite, and most organoarsenic compounds), and $^{+}5$ (As[V]: the most stable inorganic arsenic oxycompounds). Arsenic also bonds readily to itself, forming, for instance, As–As pairs in the red sulfide realgar and square As_4^{3-} ions in the arsenide skutterudite. In the $^{+}3$ oxidation state, the stereochemistry of arsenic is affected by the possession of a lone pair of electrons.

Arsenopyrite, also unofficially called mispickel, is the most common arsenic-bearing mineral. On roasting in air, the arsenic sublimes as As(III) oxide leaving iron oxides.

The most important compounds of arsenic are arsenic(III) oxide, As_2O_3, (white arsenic), the yellow sulfide orpiment (As_2S_3), and red realgar (As_4S_4), Paris Green, calcium arsenate, and lead hydrogen arsenate. The latter three have been used as agricultural insecticides and poisons. Orpiment and realgar were formerly used as painting pigments, though they have fallen out of use because of their toxicity and reactivity. Although arsenic is sometimes found native in nature, its main economic source is the mineral arsenopyrite mentioned above; it is also found in arsenides of metals such as silver, cobalt (cobaltite: CoAsS and skutterudite: $CoAs_3$), and nickel; as sulfides; and when oxidized as arsenate minerals such as mimetite, $Pb_5(AsO_4)_3Cl$, and erythrite, $Co_3(AsO_4)_2 . 8H_2O$, and more rarely arsenites ("arsenite" = arsenate(III), AsO_3^{3-} as opposed to arsenate(V), AsO_4^{3-}). In addition to the inorganic forms mentioned above, arsenic also occurs in various organic forms in the environment. Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation.

Table 8-8 presents chemical and physical properties of some of the more common forms of arsenic.

TABLE 8-8 Physical and Chemical Properties of Arsenic and Arsenic Compounds

Property	Arsenic	Arsenic Acid	Arsenic Pentoxide	Arsenic Trioxide
Molecular weight	74.9216	141.944	229.840	197.841
Color	Silver-gray or tin-white	White[a]	White	White
Physical state	Solid	Solid[b]	Solid	Solid
Boiling point	613°C sublimes	Loses H_2O at 160°C[b]	No Data	460°C
Density	5.778 g/cm^3 @ 25°C	-2.2 g/cm^3	4.32 g/cm^3	3.865 g/cm^3 (cubes) 4.15 g/cm^3 (rhombic crystals)
Solubility: water	Insoluble	302 G/L at 12.5°C[b]	2,300 g/L at 20°C	17 g/L at 16°C
Partition coefficients				
Log K_{ow}	No data	No data	No data	No data
Log K_{oc}	No data	No data	No data	No data
Vapor pressure	7.5 × 10^3 mmHg @ 280°C	No data	No data	2.47 × 10^{-4} mmHg at 25°C

Property	Calcium Arsenate	Gallium Arsenide	Disodium Arsenate	Sodium Arsenite
Molecular weight	398.072	144.64	185.91	130.92
Color	Colorless	Dark gray	Colorless[d]	White to gray-white
Physical state	Solid	Solid	Solid	Solid
Boiling point	No data	No data	No data	No data
Density	3.620 g/cm^3	5.3176 g/cm^3 25°C	1.87 g/cm[d]	1.87 g/cm^3
Solubility: water	0.13 g/L @ 25°C	<1 mg/mL at 20°C	Soluble 1:3 parts in water[d]	Freely soluble in water
Partition coefficients				
Log K_{ow}	No data	No data	No data	No data
Log K_{oc}	No data	No data	No data	No data
Vapor pressure	0 mmHg at 20°C	No data	No data	No data
pK_a	No data	No data		

Property	Arsenilic Acid	Arsenobetaine	Dimethylarsinic Acid	
Molecular weight	217.06	196.1[b]	138.00	
Color	White	No data	Colorless	
Physical state	Solid	Solid[b]	Solid	
Boiling point		No data	>200°C	
Density	1.9571 g/cm^3 at 10°C	No data	No data	

(*continues*)

TABLE 8-8 ***(continued)***

Property	Arsenilic Acid	Arsenobetaine	Dimethylarsinic Acid
Solubility: water	Slightly soluble in cold water; soluble in hot water	No data	2,000 g/L at 25°C
Partition coefficients			
Log K_{ow}	No data	No data	No data
Log K_{oc}	No data	No data	No data
pK_a	No data	2.2[c]	1.57
Vapor pressure	No data	No data	No data

Property	Methanearsonic Acid	3-Nitro-4-hydroxy-phenylarsonic Acid	Sodium Arsanilate
Molecular weight	139.97	263.03	239.04
Color	White	Pale yellow	White or creamy white
Physical state	Solid	Solid	Solid
Boiling point	No data	No data	No data
Density	No data	No data	No data
Solubility: water	256 g/L at 20°C	Slightly soluble in cold water: soluble in about 30 parts boiling water	Soluble 1 part in 3 parts water
Partition coefficients			
Log K_{ow}	No data	No data	No data
Log K_{oc}	No data	No data	No data
pK_a	$pK_{a1} = 4.1$; $pk_{a2} = 9.02$	No data	No data
Vapor pressure	$<7.5 \times 10^{-8}$ mmHg	No data	No data

Property	Disodium Methanearsonate	Sodium Dimethylarsinate	Sodium Methanearsonate
Molecular weight	183.93	159.98	161.95
Color	White	Colorless to light yellow	White
Physical state	Solid	Solid	Solid
Boiling point	No data	No data	No data
Density	1.04 g/cm^3	>1 g/cm^3 at 20°C	No data

TABLE 8-8 ***(continued)***

Property	Disodium Methanearsonate	Sodium Dimethylarsinate	Sodium Methanearsonate
Solubility: water	432 g/L at 25°C	200 g/L at 25°C	580 g/L at 20°C
Partition coefficients:			
Log K_{ow}	<1	No data	-3.10
Log K_{oc}	No data	No data	No data
$p\mathrm{K_a}$	$p\mathrm{K}_{a1} = 4.1$; $p\mathrm{K}_{a2} = 8.94$	6.29	$p\mathrm{K}_{a1} = 4.1$; $p\mathrm{K}_{a2} = 9.02$
Vapor pressure	10^{-7} mmHg	No data	7.8×10^{-8} mmHg

[a] All information from HSDB (2005), except where noted.

[b] Cannon et al. (1981) (arseonbetaine as monohydrate).

[c] Terasahde et al. (1996).

[d] Value for disodium arsenate heptahydrate.

Environmental Fate and Behavior

Arsenic can be found naturally on earth in small concentrations. It occurs in soil and minerals, and it may enter air, water, and land through wind-blown dust and water runoff. Arsenic in the atmosphere comes from various sources: volcanoes release approximately 3,000 tons per year, and microorganisms release volatile methylarsines to the extent of 20,000 tons per year, but human activity is responsible for much more: 80,000 tons of arsenic per year are released by the burning of fossil fuels.

Plants absorb arsenic fairly easily, and high concentrations may be present in food. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that contain large amounts of arsenic and will die as a result of arsenic poisoning as the fish is digested in their bodies.

Treatment

As mentioned above, arsenic is found in groundwater in the following valences: $^{-}3$, 0, $^{+}3$ (arsenite, As[III]), and $^{+}5$ (arsenite, As[V]). The $^{-}3$ and 0 valence states are rare and are not often present in groundwater. As(III) is more toxic to humans, and four to ten times more soluble than As(V). Arsenic can change its valence depending on conditions in the environment, such as pH, redox, the presence of complexing ions (sulfur, iron, and calcium, etc.), and microbial activity.[75]

The most common aboveground treatment technologies for arsenic are precipitation/coprecipitation, adsorption, ion exchange, and membrane filtration. Some research has been conducted on the aboveground biological treatment of arsenic, but the technology is still emerging. In situ treatment technologies for arsenic include permeable reactive barriers, electrokinetic processes, and phytoremediation.[76]

Precipitation/Coprecipitation

Precipitation/coprecipitation is a process that generally involves three steps: (1) adding chemical reagents to the water; (2) forming a filterable, solid matrix by precipitation, coprecipitation, or a combination of these processes; and (3) separating the solid matrix from the water.[75] Prior to adding the reagents, As(III) is frequently oxidized to As(V)—the lesser soluble form—in a pretreatment step. Oxidizing As(III) can be accomplished by ozonation, photooxidation, or by adding an oxidant such as potassium permanganate, sodium hypochlorite, or hydrogen peroxide. The first step often involves pH adjustment, and then the precipitation or coagulating agent is added. Coagulation agents [75] for arsenic treatment include the following:

- Ferric salts (ferric chloride, ferric sulfate, and ferric hydroxide, etc.)
- Ammonium sulfate
- Alum (aluminum hydroxide)
- Lime softening (limestone, calcium hydroxide)
- Magnesium sulfate
- Copper sulfate
- Sulfide

Filterable solids are filtered out of solution by a clarifier, multimedia filter, or conventional bag or cartridge filters. The resulting sludge can then be dewatered and disposed of as a solid that may be a hazardous waste. The sludge may require solidification/stabilization prior to being disposed of. Finally, the effluent stream may need pH adjustment following treatment. Precipitation/coprecipitation may be affected by the valence of arsenic being treated, pH, and the presence of some anions and/or cations.

Adsorption

Arsenic can be removed from water by adsorption onto a medium similar to VOC adsorption onto GAC and perchlorate removal onto ion exchange resin. The water is passed through a vessel of medium until the medium is saturated with arsenic and no longer has treatment capacity. When a medium has become exhausted, it is either disposed of as a solid waste or regenerated by a chemical process. The following adsorption media [75] are often used in arsenic treatment:

- Activated alumina
- GAC
- Copper–zinc granules
- Granular ferric oxide
- Ferric hydroxide-coated newspaper pulp
- Iron oxide-coated sand
- Iron filings mixed with sand
- Greensand (often referred to as oxidation/filtration)
- Surfactant modified zeolite

Activated alumina is a common drinking water treatment technology for arsenic. It can often treat 20,000 to 25,000 bed volumes of water before becoming saturated with arsenic. Activated alumina can be disposed of as a solid waste or regenerated, which produces a liquid waste that requires disposal. Regeneration is accomplished by first backwashing the media and then running a caustic solution (generally sodium hydroxide) through it. The media is neutralized with an acidic solution (generally sulfuric acid), and finally rinsed and returned to service.[75] The regeneration can produce a sludge that requires disposal as a solid waste because the acid used in the regeneration process often dissolves a portion of the activated alumina.

GAC has a limited capacity for As(V) (0.020 grams As[V] per gram of GAC) and does not effectively remove As(III).[75] GAC can be impregnated with a metal, such as iron or copper, to increase the arsenic capacity. Copper-impregnated GAC can be used to treat As(III); it has a capacity of 0.48 grams As(III) per gram of impregnated GAC.[75] Ferrous iron-impregnated GAC removes As(V) at a capacity of 0.2 grams As(V) per gram of impregnated GAC (U.S. EPA, 2002). Arsenic-laden GAC may not be effectively regenerated by conventional thermal methods because the sorbed metal may not be volatilized at the applied regeneration temperatures. Additionally, off-gas treatment may be complicated by the presence of arsenic.

Iron-based media, such as granular ferric hydroxide, ferric hydroxide-coated newspaper pulp, iron oxide-coated sand, and iron filings mixed with sand, are often used to remove arsenic from drinking water.[75] Arsenic treatment processes that utilize an iron medium are often used in combination with another technology such as oxidation, precipitation/coprecipitation, ion exchange, or filtration.[75] These media can be disposed of as solid wastes and replaced, or they can be regenerated using a process similar to activated alumina regeneration discussed above.

Greensand filtration can be used to treat arsenic. Greensand is an iron-rich mineral that is mixed with sand and treated with potassium permanganate, which forms a layer of manganese oxides. The permanganate oxidizes any As(III) to As(V), which is then adsorbed onto the media. Spent greensand can be disposed of as a solid waste and replaced or regenerated with a permanganate solution.[75]

Arsenic treatment by surfactant-modified zeolites has been tested at the laboratory-scale level and may prove to be a viable treatment technology.

Ion Exchange

Ion exchange can also be applied to arsenic treatment in a manner similar to perchlorate treatment. Generally, a strong base anion exchange resin is utilized for arsenic treatment. As with other arsenic treatment technologies, As(III) is not effectively removed by ion exchange, so oxidation to As(V) is often a pretreatment step. Next, water is filtered to remove suspended solids (5- or 10-micron filters are often used) and VOCs, if required, to prevent the ion exchange resin from becoming fouled. The water is then treated by the anion exchange media. Spent ion exchange resin can be disposed of as a solid waste and replaced with fresh resin or regenerated by an anion solution, generally the chloride anion supplied by a sodium chloride brine solution. Unlike perchlorate treatment, the majority of arsenic treatment systems are regenerable. The regeneration brine can be recycled (i.e., it can perform multiple regenerations) before it requires disposal as a liquid waste. Typical ion exchange capacities for arsenic treatment range between 300 and 60,000 bed volumes.[75] High sulfate concentration, and to a lesser extent nitrate and chloride concentrations, can greatly reduce the arsenic capacity of the anion exchange resin, which adversely affects arsenic treatment costs.

Membrane Filtration

Reverse osmosis, and to a lesser extent nanofiltration, can be utilized to remove arsenic from water. As discussed in the perchlorate section, reverse osmosis is a process where water is forced through a semi-permeable membrane, while dissolved solids are retained and concentrated into the rejectate. The rejectate must then be disposed of as a liquid waste, or it can be dehydrated and disposed of as a solid waste. Reverse osmosis is affected by suspended solids, high molecular weight dissolved solids, organic compounds, and colloids that can foul the membrane. Arsenic(V) is a larger ion that is removed more efficiently than As(III). Low water temperatures require higher reverse osmosis pressures and more membrane surface area. Membrane filtration is not a common arsenic treatment technology because it generally has a higher treatment cost than other treatment technologies [77] because of the high volume of rejectate that must be properly disposed of.

Permeable Reactive Barriers

Permeable reactive barriers can be implemented to treat arsenic-contaminated groundwater in situ. Reactive media that have been tested for arsenic treatment include ZVI, basic oxygen furnace slag, limestone, surfactant modified zeolite, and ion exchange resin.[75] In ZVI applications, groundwater reacts with the ZVI, which increases pH, lowers the Eh, and increases dissolved hydrogen concentrations.[75] The pH change precipitates calcium, iron, and insoluble metal hydroxides; the lowered Eh reduces metals and cations; and the increased dissolved hydrogen concentration stimulates microorganisms that use hydrogen, such as nitrate- and sulfate-reducing bacteria.[75] Arsenic(V) binds to the ZVI, creating a positive charge that binds arsenate to the iron by electrostatic forces. In sulfate-reducing conditions, arsenic may be precipitated as arsenic sulfide or it may be coprecipitated with ferrous sulfide.[75] Several bench-scale studies are being conducted to further investigate permeable reactive barriers with adsorptive agents such as activated alumina, bauxite, ferric oxides and oxyhydroxides, peat, humate, lignite, coal, and sulfate-modified zeolite. Precipitation barriers using ferrous hydroxide, ferrous carbonate, ferrous sulfide, limestone, and zero-valent metals are also being investigated at the bench-scale level.[75] As with any application of a permeable reactive barrier, subsurface conditions must be considered, and permeable reactive barriers can become plugged or clogged with time.

In situ Electrokinetic Treatment

In situ electrokinetic treatment of arsenic is an emerging remediation technology that can treat both soil and groundwater simultaneously. An electric charge is applied to electrodes installed in the subsurface that attracts anions and cations to the electrodes, and then the contaminants can be removed by electroplating or electrodeposition, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or pumping a fluid around the electrode.[75] Arsenic(III) and As(V) are attracted to the cathode during electrokinetic treatment. This technology can be also applied in aboveground treatment systems by precipitating/coprecipitating the arsenic and then removing the solids by filtration. The following factors can affect electrokinetic arsenic treatment: arsenic species being treated, salinity and cation exchange capacity, soil moisture, polarity and magnitude of the ionic charge, soil type, and pH.[75]

Phytoremediation

There are few data available for phytoremediation of arsenic; however, there is a full-scale phytoremediation project being conducted that will eventually produce a data set for technology evaluation.

Bioremediation

There are a very limited number of projects where arsenic is being treated biologically. Biological treatment of arsenic generally converts the arsenic to a species that is more amenable to precipitation/coprecipitation. A biological reactor has been constructed that utilizes microorganisms to deposit iron oxides on a medium where the arsenic is then adsorbed. This reactor produces an arsenic-laden biomass that must be disposed of as a solid waste.[75] Another bioreactor utilizes sulfate-reducing and arsenic-reducing bacteria to precipitate arsenic as an insoluble arsenic–sulfide complex. This bioreactor is "regenerated" by stripping the arsenic–sulfide complex from the column, and then biologically activating it.[75] Biological treatment of arsenic is affected by the following factors: pH, contaminant concentration, available nutrients, temperature, and iron concentration.[75]

Emerging Technologies

Additional research is being conducted on arsenic treatment using electrodialysis, electrodialysis reversal, and coagulation-assisted membrane processes. Research is also being conducted on combinations of arsenic treatment technologies, such as adding ferric salts to water and treating the solution in a bioreactor, this approach reduces treatment costs, coagulant requirement, and sludge generation.[78]

HEXAVALENT CHROMIUM

History and Background

Chromium (Cr) is a metallic element that occurs naturally in the trivalent, Cr(III), and hexavalent, Cr(VI), forms. The divalent state, Cr(II), is relatively unstable and is readily oxidized to the trivalent state.

$$\mathrm{Cr}^{6+}$$

HEXAVALENT
CHROME

FIGURE 8-7. Hexavalent chrome.

Elemental chromium, Cr(0) does not occur naturally. The hexavalent form is the second most stable but is found in nature only in the rare mineral crocoite. The trivalent state is the most stable form and is the most prevalent form found in nature.

Chromium(III) is an essential nutrient that helps the body utilize sugars, proteins, and fats. Chromium picolinate, a trivalent form of chromium, is used as a dietary supplement to speed metabolism; it may also have antidiabetic effects. It has also been shown to be absorbed more readily than chromium from food sources.

Hexavalent chromium, or Cr(VI), compounds are those that contain the element chromium in the $^{+}6$ oxidation state. Chromates are often used as pigments for photography and in pyrotechnics, dyes, paints, inks, and plastics. They can also be used for stainless-steel production, textile dyes, wood preservation, leather tanning, and as anti-corrosion and conversion coatings.

Hexavalent chromium is recognized as a human carcinogen by way of inhalation. Workers in many different occupations are exposed to hexavalent chromium. Occupational exposures occur mainly among the following types of workers who

- Handle dry chromate-containing pigments
- Spray chromate-containing paints and coatings
- Operate chrome-plating baths
- Weld, cut, or grind chromium-containing metals such as stainless steel

Breathing high concentrations of chromium(VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum.

Ingesting a large quantity of chromium(VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium(VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium(VI) or chromium(III). Allergic reactions consisting of severe redness and swelling of the skin have been noted.[79]

Chromium Characteristics

Trivalent chromium compounds, with a few exceptions, are generally insoluble in water. Hexavalent compounds such as the ammonium and alkali salts of chromic acid tend to be more soluble in water. The alkaline metal salts (calcium, strontium) of chromic acid are much less soluble in water. The hexavalent chromium compounds are reduced to the more stable, and less soluble, trivalent form in the presence of oxidizable organic matter. In natural waters with low concentrations of reducing materials (i.e., organic matter), such as groundwater, hexavalent chromium compounds are more stable. The physical and chemical properties of various chromium compounds are presented in Table 8-9.[79]

Regulatory Framework

Currently, the U.S. EPA has established an MCL for chromium of 100 m µg/L. This standard is for total chromium and includes all valences dissolved in drinking water. Because trivalent chromium is significantly less toxic than the hexavalent form, there is now pressure to establish an MCL specifically for the hexavalent form of chromium.

The Occupational and Safety Health Act regulates hexavalent chromium in the workplace as an airborne concern, recognizing that inhalation is a significant exposure route for hexavalent chromium. Currently, no state regulates hexavalent chromium specifically in drinking water, although California is in the process of establishing an MCL for hexavalent chromium.

In 1999, as part of the process of reviewing MCLs in response to public health goals, California's Department of Health Services identified the chromium MCL as one for review. In particular, the Department of Health Services sought to determine whether an MCL that is specific for hexavalent chromium would be appropriate.

Subsequently, events primarily between 1999 and 2001 and concerns about hexavalent chromium's potential carcinogenicity when ingested resulted in a state law that was enacted requiring the Department of Health Services to adopt a chromium(VI)-specific MCL.

In California, hexavalent chromium is currently regulated under the 50-µg/L MCL for total chromium. The total chromium MCL is considered protective of public health for hexavalent chromium, which is considered to be the more toxic form of chromium.

TABLE 8-9 Physical and Chemical Properties of Chromium and Chromium Compounds[a]

Property	Chromium(0)	Chromium(III) Acetate, Monohydrate	Chromium(III) Nitrate, Monohydrate	Chromium(III) Chloride
Molecular weight	51.996	247.15	400.15	158.36
Color	Steel-gray	Gray-green or bluish-green	Purple or violet	Violet or purple
Physical state	Solid	Solid	Solid	Solid
Boiling point	2,672°C	No data	Decomposes at 100°C	Sublimes at 1,300°C
Density (g/cm^3)	7.20 (28°C)[b]	No data	No data	2.76 (15°C)[b]
Solubility: water	Insoluble	Soluble	Soluble	Slightly soluble in hot water
Partition coefficients				
Log K_{ow}	No applicable	No applicable	No applicable	No applicable
Log K_{oc}	No applicable	No applicable	No applicable	No applicable
Vapor pressure	1 mmHg @ 1,616°C	No data	No data	No data

Property	Chromium(III) Chloride Hexahydrate	Ferrochromite (Chromium[III])	Chromium(III) Oxide	Chromium(III) Phosphate
Molecular weight	266.45			
Color	Violet	Brown-black	Green	Gray-brown to black[d]
Physical state	Solid	Solid	Solid	Solid
Boiling point	No data	No data	4,000°C	No data
Density (g/cm^3)	1.76[c]	4.97 (20°C)	5.21[c]	2.94 (32.5°C)[b,d]
Solubility: water	58.5 g/100 mL @ 25°C	Insoluble	Insoluble	Insoluble[d]
Partition coefficients				
Log K_{ow}	No data	No applicable	No applicable	No applicable
Log K_{oc}	No data	No applicable	No applicable	No applicable
Vapor pressure	No data	No data	No data	No data

Property	Chromium(III) Sulfate	Sodium Chromite (Chromium[III])	Chromium(IV) Oxide	Ammonium Dichromate (Chromium[VI])
Molecular weight	392.16	106.98	83.99	252.06
Color	Violet or red	No data	Brown-black	Orange
Physical state	Solid	No data	Solid	Solid
Boiling point	No data	No data	Not applicable	Not applicable
Density (g/cm^3)	3.012[c]	No data	No data	2.15 (25°C)[b]
Solubility: water	Insoluble	No data	Insoluble	30.8 $g/100\,cm^3$ @ 15°C
Partition coefficients				
Log K_{ow}	No applicable	No applicable	No applicable	No applicable
Log K_{oc}	No applicable	No applicable	No applicable	No applicable
Vapor pressure	No data	No data	No data	No data

(*continues*)

TABLE 8-9 ***(continued)***

Property	Calcium Chromate (Chromium[VI])	Chromium(VI) Trioxide	Lead Chromate (Chromium[VI])	Potassium Chromate (Chromium[VI])
Molecular weight	156.01	99.99	323.18	194.20
Color	Yellow	Red	Yellow	Yellow
Physical state	Solid	Solid	Solid	Solid
Boiling point	No data	Decomposes	Decomposes	No data
Density (g/cm^3)	2.89[c]	2.70 (25°C)	6.12 (15°C)	2.732 (18°C)
Solubility: water	2.23 g/100 mL[c]	61.7 g/100 mL @ 0°C	5.8 μg/100 mL	62.9 g/100 mL @ 20°C
Partition coefficients				
Log K_{ow}	No applicable	No applicable	No applicable	No applicable
Log K_{oc}	No applicable	No applicable	No applicable	No applicable
Vapor pressure	No data	No data	No data	No data

Property	Potassium Dichromate (Chromium[VI])	Chromate Chromate (Chromium[VI])	Sodium Dichromate, Dehydrate (Chromium[VI])
Molecular weight	294.18	161.97	298.00
Color	Red	Yellow	Red
Physical state	Solid	Solid	Solid
Boiling point	Decomposes at 500°C	No data	Decomposes at 400°C
Density (g/cm^3)	2.676 (25°C)	2.710–2.736[c]	2.52 (13°C)
Solubility: water	4.9 g/100 mL @ 0°C	87.3 g/100 mL @ 30°C	230 g/10 mL @ 0°C
Partition coefficients			
Log K_{ow}	No applicable	No applicable	No applicable
Log K_{oc}	No applicable	No applicable	No applicable
Vapor pressure	No data	No data	No data

Property	Strontium Chromate (Chromium[VI])	Zinc Chromate (Chromium[VI])	Chromium(III) Picolinate
Molecular weight	203.61	181.97	418.3[d]
Color	Yellow	Lemon-yellow	Ruby red[d]
Physical state	Solid	Solid	Crystal[d]
Boiling point	No data	No data	No data
Density (g/cm^3)	3.895 (15°C)	3.40[c]	No data
Solubility: water	0.12 g/100 mL @ 15° C)	Insoluble	1 ppm @ 25°C
Partition coefficients			
Log K_{ow}	No applicable	No applicable	1.753[e]
Log K_{oc}	No applicable	No applicable	No data
Vapor pressure	No data	No data	No data

[a] Hartford (1979) Weast (1985), except when noted.

[b] Temperature at which the densities were measured has been given only when such data are available.

[c] Temperature at which density was measured was not specified.

[d] Broadhurst et al. (1997).

[e] Chakov et al. (1999).

Note. DMSO, dimethylsulfoxide.

California's MCL was established in 1977, when the Department of Health Services adopted what was then a "National Interim Drinking Water Standard" for chromium. The U.S. EPA adopted the same standard but in 1991 raised the federal MCL to 100 μg/L. California did not follow U.S. EPA's lead and has maintained its 50-μg/L MCL for total chromium.

California's Health and Safety Code guided the development of an MCL for hexavalent chromium by January 1, 2004; however, the Office of Environmental Health Hazard Assessment, the agency that must set public health goals prior to establishing an MCL, requested a delay until certain scientific studies on hexavalent chromium toxicity were completed. As a result, the public health goal for hexavalent chromium is not yet available, so the Department of Health Services cannot proceed with the MCL process.

Environmental Fate and Behavior

Chromium speciation in groundwater is dependent on the redox and the pH conditions of the aquifer. The hexavalent form is predominant under highly oxidizing conditions, while the trivalent form predominates in reducing conditions. Given the low solubility of the trivalent forms of chromium, it is expected that dissolved concentrations of total chromium in aquifers with reducing conditions would be very low. On the other hand, aquifers that favor oxidizing conditions would tend to have the potential to sustain higher dissolved concentrations of hexavalent chromium compounds. Oxidizing conditions are generally found in shallow aquifers or in aquifers located in arid environments. As a result, hexavalent chromium plumes in groundwater located in arid environments may persist for significant periods of time.

Hexavalent chromium has been shown to be reduced naturally in the environment by sulfide and ferrous iron present in the soil, as well as by microbial reduction.[79] Therefore, the ability of chromium to migrate in groundwater is directly related to the redox potential, pH, geochemistry, and microbial communities present in the aquifer.

Treatment

As discussed above, chromium is present in groundwater as two different species: (1) hexavalent chromium (Cr^{6+} or Cr[VI]); and (2) trivalent chromium (Cr^{3+} or Cr[III]). Cr(VI) is acutely toxic, mutagenic, and carcinogenic and is the more soluble and mobile of the two species.[80] The trivalent, reduced form, Cr(III), is much less toxic and is generally immobile in groundwater that is moderately alkaline to slightly acidic.[80]

Coagulation/Filtration

As with other heavy metals, Cr(VI) can be treated with conventional methods like coagulation/filtration. This process is performed by adding an acid (e.g., sulfuric acid) to the solution to reduce the pH to between 2 and 3, adding a reductant (sodium sulfite, sodium metabisulfite, sulfur dioxide gas, etc.) to reduce the Cr(VI) to Cr(III), and then adding a base to increase the pH and precipitate the Cr(III) as chromium hydroxide.[81] This process requires a large quantity of acid, reductant, and base and generates a large volume of sludge that must be disposed of as a solid waste. Finally, this process produces treated water with a high sulfate concentration. For example, if the influent water has a sulfate concentration of 34 mg/L, the treated water will have a sulfate concentration of approximately 1,700 mg/L.[82]

Ion Exchange

Ion exchange can be used as a treatment technology to treat Cr(VI). A strong base type I quaternary ammonium anion exchange resin, such as Purolite A-600, can be used as a brine-regenerated medium.[83] Regeneration is accomplished by first backwashing the ion exchange bed, then flowing two bed volumes of a 15.8-percent brine solution in the countercurrent direction at a flow rate of approximately 0.2 gpm per cubic foot of bed volume (gpm/ft^3), and finally rinsing with approximately two bed volumes of water.[83] The brine regenerant can subsequently be treated to remove the Cr(VI) and then be recycled as the regenerant solution, or it can be disposed of as a liquid waste.

Biological

Chung et al.[84] demonstrated that Cr(VI) could be reduced to Cr(III) in a hydrogen-based membrane biofilm reactor simultaneously with selenate, the oxidized form of selenium, Se(VI). This reactor (described in the perchlorate treatment section of this chapter) utilizes gaseous hydrogen as the electron donor and produces nitrate-reducing conditions. Two studies were conducted with the membrane biofilm reactor using an artificial, spiked groundwater that was composed of 5 mg/L of nitrate (as nitrogen), 78.5 mg/L of sulfate, and 250 μg/L of oxidized chromium (chromate, Cr[VI]) or selenium (selenate, Se[VI]). In the first study, selenate was fed to the reactor to test selenium reduction, and then the reactor was switched to chromate. In the second test, chromate was the initial species tested, and then the reactor was switched to selenate. During the first study after the reactor reduced selenate for 50 days, chromate was fed to the reactor and immediately began being reduced to Cr(III). After 20 days of operation, no Cr(III) was observed in the effluent, and all chromium species concentrations were <10 μg/L. In the second study, chromate was initially fed to the membrane biofilm reactor, and Cr(VI) was reduced to Cr(III), but the reduced chromium was not retained on the biofilm like it was in the first study. The second study indicated that most of the reduced chromium was not the insoluble hydroxide form that would have been retained in the biofilm; this may have been caused by complexation with phosphate (which was at a higher concentration than average groundwater), sulfate, or organic ligands.[84] The studies did illustrate that Cr(VI) can be effectively reduced to Cr(III) in a membrane biofilm reactor.

Emerging Technologies

Research at the University of Oklahoma has been conducted on polyelectrolyte-enhanced ultrafiltration for the treatment of aqueous Cr(VI). This process enables ultrafiltration to be used as a treatment technology in lieu of reverse osmosis. In the polyelectrolyte-enhanced ultrafiltration process, a polymer is added to the water that forms a colloid with chromate (Cr[VI]), which is then removed by ultrafiltration. The colloidal surfactant/chromate retentate is then treated with barium chloride, which precipitates barium sulfate and barium chromate, which is disposed of as a solid waste.[82]

In situ Treatment

Chrome(VI) can be treated in situ by the following methods:

- Geochemical fixation
- Permeable reactive barriers
- IRZs
- Soil flushing/chromium extraction
- Electrokinetics
- Phytoremediation

Geochemical Fixation

Geochemical fixation is an in situ process that reduces Cr(VI) to Cr(III), which is in turn adsorbed onto the soil matrix, rendering it immobile in groundwater. This process is generally accomplished by pumping contaminated groundwater to the surface, removing the chromium(VI), amending it with a reductant, and then reinjecting it into the subsurface. Sulfides (e.g., calcium polysulfide) and sulfites (sodium metabisulfite, etc.) are commonly used as reductants, but they do require that ferrous iron (Fe[II]) be present as a catalyst.[80] The pH of the aquifer may need to be reduced prior to injecting a reductant. Iron fouling near the injection point and formation of chromium hydroxides may "clog" the aquifer.

Permeable Reactive Barriers

Permeable reactive barriers are also being used to treat Cr(VI). They are generally applied in either the funnel-and-gate or in a continuous trench configuration. ZVI, sodium dithionite, and zeolite-based media have been utilized as Cr(VI) permeable reactive barrier media. At a pH typical of groundwater (6 to 9), Cr(III) tends to precipitate as chromium hydroxide; in the presence of iron, it generally precipitates as a mixed chromium-iron hydroxide solution.[85]

In situ Reactive Zone

An IRZ, discussed in Chapter 4, can also be used to create reducing conditions in the aquifer to reduce Cr(VI) to Cr(III). IRZ mechanisms can be abiotic or biotic. Abiotic pathways include reduction, oxidation, precipitation, and sorption. Biotic pathways include reduction, oxidation, precipitation, biosorption, bioaccumulation, organo-metal complexation, and phytoremediation.[86] Molasses, ZVI, and ferrous sulfate have been used in Cr(VI) IRZ applications.

Soil Flushing

Soil flushing can be used as an in situ treatment technology for Cr(VI). This technology is applied by injecting a flushing solution into the groundwater that mobilizes the Cr(VI), which is then extracted from the aquifer, treated to remove the recovered Cr(VI), and then amended with a reagent(s) and reinjected as the flushing solution. Surfactants have been used as a flushing fluid reagent, and research is being conducted with acids, bases, chelating agents, and surfactants/co-solvents as possible reagents.[80]

Emerging Technologies

Electrokinetic remediation of Cr(VI), similar to the As(III) treatment discussed earlier in this chapter, is an innovative treatment technology that is being tested at the field-scale level.[80] Phytoremediation of Cr(VI)-contaminated groundwater may also be applicable at sites with low concentrations of Cr(VI) in shallow groundwater, but few data are currently available for Cr(VI).

1,2,3-TRICHLOROPROPANE

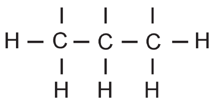
Background and History

1,2,3-Trichloropropane was used historically as a paint and varnish remover, a cleaning and degreasing agent, a cleaning and maintenance solvent, and, more recently, a chemical intermediate.[87] Its use as a pesticide was in formulations with dichloropropenes in the manufacture of D-D, a soil fumigant. 1,2,3-Trichloropropane has various industrial uses and historical pesticide uses, with the primary possible contaminating activity appearing to be hazardous waste sites and through the use of soil fumigants.

California's Department of Health Services established a notification level for 1,2,3-trichloropropane in 1999 after it was discovered at the Burbank Operable Unit—a southern California Superfund site—because of concerns that the chemical could be present in drinking water supplies. The notification level was established at 0.005 μg/L (5 parts per trillion or 5 ng/L), which created some problems for analysis because a method did not exist to reliably measure 1,2,3-trichloropropane at that concentration. The Department of Health Services developed a method to analyze 1,2,3-trichloropropane at the 5-ng/L level in 2000 and required water agencies to monitor for the compound in 2001. Although monitoring had occurred from 1989 through the late 1990s under an earlier regulation, fewer than 20 drinking water sources had reported detections. The lack of detection was likely caused by the method detection limit at the time, which was 0.05 μg/L. With the development of the more sensitive method, California undertook a monitoring program for their water systems in 2001. As of August 2, 2006, eighty-five water systems in California had reported detections (two or more) from 303 sources.

1,2,3-Trichloropropane Characteristics

1,2,3-Trichloropropane is a clear, colorless to straw-colored liquid with a strong acrid odor. It has a boiling point of 156°C and a vapor pressure



$$H-\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-H$$

1,2,3-TRICHLOROPROPANE

FIGURE 8-8. 1,2,3-Trichloropropane.

of 3 mmHg. 1,2,3-Trichloropropane is considered slightly soluble in water (1,750 mg/L). It has a log soil-adsorption coefficient in sandy or silty loam of 77 to 95 (which indicates that under environmental conditions it is prone to washing out of soil). The log octanol–water partition coefficient for 1,2,3-trichloropropane is reported to be 2.54[88], which would indicate that the compound would be amenable to activated carbon treatment; however, for reasons presented below, the compound is not readily treated using activated carbon. The Henry's law constant for 1,2,3-trichloropropane has been calculated at 3.17×10^{-4} atm-m^3 M^{-1} (ATSDR, 1992), which would indicate that 1,2,3-trichloropropane is unlikely to volatilize from water or be removed by air stripping.

Regulatory Framework

1,2,3-Trichloropropane is regulated in the United States under the Clean Air Act, the Emergency Planning and Community Right-to-Know Act (as part of the Toxic Release Inventory), and the Resource Conservation and Recovery Act (as a hazardous constituent of waste). While there is no federal drinking water standard for 1,2,3-trichloropropane, the U.S. EPA recommends that adults should avoid drinking water containing more than 2 μg/L of 1,2,3-trichloropropane for a sustained period (seven years). The U.S. EPA region IX preliminary remediation goal for tap water has been set at 0.0056 μg/L. 1,2,3-Trichloropropane is regulated as a compound that is reasonably anticipated to be a human carcinogen based on sufficient evidence of malignant tumor formation at multiple sites in multiple species of experimental animals.

California has led the way in regulation of 1,2,3-trichloropropane. The development of a more sensitive analytical method and the subsequent drinking water source survey that California conducted in 2001 found that a significant number of drinking water sources contained detectable concentrations of 1,2,3-trichloropropane. Given the frequency of detection and the relative toxicity of this compound, California has determined that 1,2,3-trichloropropane is a candidate for regulation. A notification level of 0.005 μg/L has been established in California. The next step will be to publish an MCL for the compound. The publication of the MCL is expected to take several years, and the notification level will serve as the regulatory guidance in the interim.

Environmental Fate and Behavior

1,2,3-Trichloropropane is prone to washing out of soil under typical environmental conditions. This fact is borne out by the appearance of 1,2,3-trichloropropane in groundwater after nematocides containing 1,2,3-trichloropropane are applied to soil. It also explains the preponderance of groundwater wells with 1,2,3-trichloropropane found in agricultural areas in California.

1,2,3-Trichloropropane does not appear to be readily biodegradable. Studies show that 1,2,3-trichloropropane may be cometabolically degraded by methanotrophs. To date, no organisms have been identified that can use 1,2,3-trichloropropane as a sole carbon source. As a result, 1,2,3-trichloropropane is likely to persist in the environment for long periods of time.

Treatment

Information sources on treatment technologies for 1,2,3-trichloropropane, a relatively new contaminant, are limited at this time. Because of its low Henry's law constant, air stripping is not an effective treatment technology.

Biodegradation

No data were found supporting natural attenuation of 1,2,3-trichloropropane, but it may be possible under favorable conditions because of the half-life in acclimated aerobic soil grab samples between six months and one year.[90] A bacterial strain created by random mutagenesis of haloalkane dehalogenase and genetic engineering of a chloropropanol-utilizing bacteria was created that can grow on 1,2,3-trichloropropane. However, numerous attempts to enrich 1,2,3-trichloropropane-degrading organisms from environmental samples or degrading 1,2,3-trichloropropane in a flow-through column have been unsuccessful.[91] The studies did, however, illustrate that biodegradation of 1,2,3-trichloropropane is at least feasible. Subsequent studies with the membrane biofilm reactor with gaseous hydrogen as the electron donor successfully reduced 0.95 μg/L of 1,2,3-trichloropropane and 0.059 μg/L of dibromochloropropane to 0.059 and <0.01 μg/L, respectively.[92]

Adsorption

Based on its chemical properties, 1,2,3-trichloropropane should be readily removed from water by liquid-phase GAC adsorption. In practice, 1,2,3-trichloropropane has a much higher GAC usage rate than predicted by modeling. This unexpected behavior may in part be caused by the long mass transfer zone exhibited by this compound.[93]

1,2,3-Trichloropropane is being treated at the Burbank Operable Unit (Burbank, California) by a drinking water treatment system that utilizes air stripping and GAC adsorption.[94] The air-stripping component of the treatment system removes a negligible amount of 1,2,3-trichloropropane, but the liquid-phase GAC effectively removes 1,2,3-trichloropropane from groundwater.

Advanced Oxidation

Advanced oxidation by an Applied Process Technology's HiPOx system demonstrated effective, simultaneous treatment of 1,2,3-trichloropropane and dibromochloropropane. The HiPOx treatment system uses ozone and hydrogen peroxide to form the hydroxyl free radical that in turn oxidizes organic compounds. Bench-scale studies reduced 0.95 μg/L of 1,2,3-trichloropropane and 0.059 μg/L of dibromochloropropane to 0.0004 μg/L and 0.001 μg/L, respectively. Additional research must be conducted to determine the destruction pathway to determine potential by-product formation and toxicity.[95] At this time, GAC is the state-of-the-art treatment technology for 1,2,3-trichloropropane.

References

1. Jacobs, J., Guertin, J., and Herron, C., Eds. Report & recommendations on the effect of MTBE on soil and ground water resources, Point Richmond, California: Independent Environmental Technical Evaluation Institute, 1999.
2. California Environmental Protection Agency, An Overview of the Use of Oxygenates in Gasoline, State of California Air Resources Board, 1998.
3. U.S. EPA. "MTBE Fact Sheet No. 3, Use and Distribution of MTBE and Ethanol," EPA 510-F-97-016, January 1998.
4. Johnson, R., Pankow, J., Bender, D., Price, C., and Zogorski, J. "MTBE to What Extent Will Past Releases Contaminate Community Water Supply Wells?" Environ. Sci. Technol., 34, pp. 210A–217A, 2000.
5. Nichols, E.M., M.D., Einarson, and S.C., Beadle. "Strategies of Characterizing Subsurface Releases of Gasoline Containing MTBE," API Publication No. 4699, American Petroleum Institute, February 2000.
6. Martinson, M., and J., Davidson, "Analysis of MTBE Groundwater Cleanup Costs", A Report to the American Petroleum Institute, June 2005, http://api-ec.api.org/filelibrary/APIAnalysisMTBECosts7-2005.pdf.
7. U.S. EPA. "Announcement of the Drinking Water Contaminant Candidate List; Notice," Federal Register, p. 10274, March 2, 1998.
8. U.S. EPA, "Final Revisions to the Unregulated Contaminant Monitoring Regulation," Office of Water, EPA 815-F-99-005, August 1999.

9. Northeast States for Coordinated Air Use Management (NESCAUM). Attachment II: MTBE in Ground and Surface Waters of the NESCAUM Region, August 1999.
10. NESCAUM, RFG/MTBE: Findings and Recommendations, August 1999.
11. Mackay, D., Wilson, R., Durrant, G., Scow, K., Smith, A., Chang, D., and Fowler, B, Pre-Prints Environmental Chemistry Division, American Chemical Society, pp. 284–286, March 2000.
12. Calgon Carbon Corporation, Product Bulletin Filtrasorb® 600, 1999.
13. U.S. EPA, "Technologies For Treating MTBE and Other Fuel Oxygenates," May 2004.
14. ITRC (Interstate Technology & Regulatory Council), "Overview of Groundwater Remediation Technologies for MTBE and TBA", Washington, D.C.: Interstate Technology & Regulatory Council, Perchlorate Team, (http://www.itrcweb.org), February 2005.
15. Koenigsberg, S. "The use of ORC in the bioremediation of MTBE," Pre-Prints Environmental Chemistry Division, American Chemical Society, pp. 289–291, March 2000.
16. Cater, S.R., Dussert, B.W., and Megonnell, N., "Reducing the Threat of MTBE-Contaminated Groundwater," Pollution Engineering, pp. 36–39, May 2000.
17. Bowman, R.H., "HiPOx Advanced Oxidation of TBA and MTBE in Contaminated Groundwater", Contaminated Soils, Sediments, and Water: Science in the Real World, Eds. Calabrese, E., Kostecki, P., and Dragun, J., Springer, 2004.
18. Schreier, C.G. "Removal of MTBE and other petroleum hydrocarbons from water using Fenton's reagent," Pre-Prints Environmental Chemistry Division, American Chemical Society, pp. 242–243, March 2000.
19. Halverson, J.E., Dutkus, K., Leister, M., Nyman, M., and Komisar, S., "Advanced oxidation of MTBE and ETBE using a peroxy-acid process," Pre-Prints Environmental Chemistry Division, American Chemical Society, pp. 236–237, March 2000.
20. McMillan. S. and Schnoor, "Phytoremediation of Methyl Tert-Butyl Ether by Hybrid Poplar Trees," Abstr. Pap. Am. Chem. Soc. 219(1), 2000.
21. U.S. EPA, "OPPT Chemical Fact Sheets — 1,4-Dioxane Fact Sheet: Support Document (CAS No. 123-9-1)," EPA 749-F-95-010, February 1995.
22. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. "Toxicological Profile for 1,4-Dioxane." July 2006.
23. National Safety Council (NSC), "Environmental Writer — 1,4-Dioxane (C4H8O2) Chemical Backgrounder," Environmental Health Center, http://www.nsc.org/ehc/ew/chems/dioxane.htm, July 1, 1997.
24. Jackson, R.E. and Dwarakanath, V., "Chlorinated Degreasing Solvents: Physical-Chemical Properties Affecting Aquifer Contamination and Remediation," Ground Water Monitoring Remediation, 19, No. 4, Fall 1999.

25. Archer W.L., "A Laboratory Evaluation of 1,1,1-Trichloroethane-metal-inhibitor Systems," Werkstoffe und Korrosion 35, 1984.
26. Brown, W.H., and Foote, C.S., Organic Chemistry, 2*nd* edition, Saunders College Publishing, Fort Worth, Texas, 1998.
27. Environmental Defense Scorecard (EDS), "Chemical Profile for 1,4-Dioxane (CAS Number 123-91-1)," http://www.scorecard.org/chemical-profiles/summary.tcl?edf_substance_id = 123%2d91%2d1, Search date-September 6, 2007.
28. Code of Federal Regulations, 29CFR 1910. 000.
29. U.S. EPA, "Health Advisory p-Dioxane," D-288, March 31, 1987.
30. U.S. EPA, "Integrated Risk Information System (IRIS) Substance File –1,4-Dioxane, CASRN 123-91-1," http://www.epa.gov/ngispgm3/iris/subst/0326.htm," On-line August 22, 1988, Revised September 1, 1990.
31. Howard, P.H., Boethling, R.S, Jarvis, W.F., Meylan, W.M., and Michalenko, E.M., "Handbook of Environmental Degradation Rates," Lewis Publishers, Inc., Chelsea, Michigan, 1991.
32. Howard, P.H. (ed.), Volume II, Solvents, In: Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Lewis Publishers, Inc., Chelsea, Michigan, 1990.
33. Nyer, E., Boettcher, G., and Morello, B., "Using the Properties of Organic Compounds to Help Design a Treatment System," Ground Water Monitoring Review 11, No. 4, 1991.
34. Priddle, M.W. and R.E. Jackson, "Laboratory Column Measurement of VOC Retardation Factors and Comparison with Field Values," Groundwater 29, No. 2, 1991.
35. U.S. EPA, "1,4-Dioxane 123-91-1," Technology Transfer Network (TTN) Web, Office of Quality Planning and Standards (OAQPS), " http://www.epa.gov/ttnuatw1/hlthef/dioxane.html," May 18, 1998.
36. McGuire, M.J., Suffet, I.H., and Radziul, J.V., "Assessment of Unit Processes for the Removal of Trace Organic Compounds from Drinking Water," J. Am. Water Works Assoc. 10, 565–572, 1978.
37. Johns, M.M., Marshall, W.E., and Toles, C.A., "Agricultural By-Products as Granular Activated Carbons for Adsorbing Dissolved Metals and Organics," J. Chem. Technol. Biotechnol. 71, 131–140, 1998.
38. Nyer, E.K., Kramer, V., and Valkenburg, N., "Biochemical Effects on Contaminant Fate and Transport," Groundwater Monitoring Review, 11, Spring 1991.
39. Calgon Carbon Corporation, "The AOT Handbook," October 1996.
40. Calgon Carbon Corporation, "UV/Oxidation Treatment of 1,4-Dioxane in Groundwater, Chemical Manufacturer, North Carolina," February 1997.
41. Grady, C.P.L., Sock, S.M., and Cowan, R.M., Biotreatability Kinetics: A Critical Component in the Scale-up of Wastewater Treatment Systems, Biotechnology in the Sustainable Environment, Ed. Sayler, G.S., Plenum Press, New York: 1997.

42. Sock, S.M., "A Comprehensive Evaluation of Biodegradation as a Treatment Alternative for Removal of 1,4-Dioxane." M.S. Thesis, Clemson University, Clemson, South Carolina, 1993.
43. Morin, M.D., "Degradative Characterization of a Mixed Bacterial Culture Capable of Mineralizing 1,4-Dioxane and Preliminary Identification of Its Isolates," M.S. Thesis, Microbiology, Clemson University, Clemson, South Carolina, 1995.
44. CH2M Hill, "1,4-Dioxane Treatment Guidance Document," Report to Hoechst Celanese Corporation, Charlotte, North Carolina, 1994.
45. Zenker, M. J., "Biodegradation of Cyclic and Alkyl Ethers in Subsurface and Engineered Environments," Dissertation., North Carolina State University, Raleigh, North Carolina, 2000.
46. Zenker, M.J., Borden, R.C., and Barlaz, M.A., "Investigation of the Intrinsic Biodegradation of Alkyl and Cyclic Ethers," Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds, Eds. Alleman, B.C. and Leeson, A.L., Battelle Press, Columbus, 1999.
47. Schnoor, J. and Alvarez, P.J.J., "Feasibility of Phytoremediation for Treatment of 1,4-Dioxane at Sites Using Hybrid Poplar Trees," A Research Proposal Submitted to Hoechst Celanese Corporation, 1996.
48. Aitchison, E.W., Kelley, S.L., Schnoor, J.L., and Alvarez, P.J.J., "Phytoremediation of 1,4-Dioxane by Hybrid Poplars," Proc. Water Environment Federation 70th Annual Meeting and Exposition, October 18-22, North Chicago, Illinois, 1997.
49. Aitchison, E.W., Kelley, S.L., Alvarez, P.J.J., and Schnoor, J.L., "Phytoremediation of 1,4-Dioxane by Hybrid Poplars," Water Environ. Res. 72, 313–321, 2000.
50. Kelly, S.L., Aitchison, E.W., Schnoor, J.L., and Alvarez, P.J.J., "Bioaugmentation of Poplar Roots with Amycolata sp. CB1190 to Enhance Phytoremediation of 1,4-Dioxane," Phytoremediation and Innovative Strategies for Specialized Remedial Applications, Eds. Alleman, B.C., and Leeson, A.L., Battelle Press, Columbus, 1999.
51. GeoSyntec Consultants, "Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater," Prepared for the Strategic Environmental Research and Development Program (SERDP). May 5, 2005.
52. U.S. EPA "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization Based on Emerging Information," National Center for Environmental Assessment, "http://www.epa.gov/ncea/perch.htm," April 1999.
53. University of California, Irvine (UCI), "Perchlorate in Drinking Water: A Science and Policy Review. Urban Water Research Center, Irvine, California June 2004.
54. U.S. FDA "Perchlorate Questions and Answers" found online at http://www.cfsan.fda.gov/~dms/clo4qa.html.

55. Gu, B., Brown, G., Maya, L., Lance, M.J., and Moyer, B., "Regeneration of Perchlorate (ClO4-)-Loaded Anion Exchange Resins by a Novel Tetrachloroferrate (FeCl4-) Displacement Technique," Environmental Science & Technology, Vol. 35, No. 16, pp. 3363–3368, 2001.
56. Gu, B., Ku, Y., and Brown, G.W., "Treatment of Perchlorate-Contaminated Groundwater Using Highly Selective, Regenerable Ion-Exchange Technology: A Pilot-Scale Demonstration," Federal Facilities Environmental Journal, 2003.
57. Gu, B., Dong, W., Brown, G., and Cole, D., "Complete Degradation of Perchlorate in Ferric Chloride and Hydrochloric Acid under Controlled Temperature and Pressure," Environmental Science & Technology, Volume 37, Number 10, Pages 2291–2295, 2003.
58. National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, California, "Final: Perchlorate (ClO4-) Treatment Technologies Literature Review Operable Unit 1 Expanded Treatability Study", June 2006.
59. Parette, R., and Cannon, F.S., Submitted to Water Research, 2005.
60. Best Technology Company, "Field Pilot Testing of a Proprietary Reverse Osmosis System Combined with Biotreatment for Removal of Perchlorate from Groundwater at the GET-B Well Site," Report to NASA, March, 2005.
61. Giblin, T., Herman, D., Deshusses, M.A., and Frankenberger Jr., W.T., "Removal of Perchlorate in Ground Water with a Flow-Through Bioreactor," Journal of Environmental Quality, 29, 2000.
62. Rittmann, B.E., Nurenberg, R., Gillogly, T.E., Lehman, G.E., and Adham, S.S., "Perchlorate Reduction Using the Hollow-Fiber Membrane Biofilm Reactor," Proceedings from the Seventh International Symposium on In-situ and On-Site Bioremediation, Orlando, Florida, 2003.
63. EcoMat, Inc., "Laboratory Studies and Bench-Scale Bioreactor Tests to Investigate Simultaneous Removal of Perchlorate and Hexavalent Chromium from Impacted Groundwater," February 2006.
64. Nzengung, V.A., Wang, C., Harvey, G., McCutcheon, S., and Wolfe, L. "Phytoremediation of Perchlorate Contaminated Water: Laboratory Studies," Phytoremediation and Innovative Strategies for Specialized Remedial Applications, April 1999.
65. Owsianiak, L.M., Lenzo, F., and Molnaa, B., "In-situ Removal of Perchlorate from Perched Groundwater by Inducing Enhanced Anaerobic Conditions," Proceedings from the Seventh International Symposium on In-situ and On-Site Bioremediation, Orlando, Florida, June 2003.
66. U.S. EPA, "Perchlorate Treatment Technology Update, Federal Facilities Forum Issue Paper," May 2005.
67. National Toxicology Program (NTP), "N-Nitrosodimethylamine CAS No. 62-75-9," Eighth Report on Carcinogens, 1998 Summary, Public Health Service, U.S. Department of Health and Human Services, 1998.

68. Nyer, E.K., Palmer, P.L., Carman, E.P., Boettcher, G., Bedessem, J.M., Lenzo, F., Crossman, T.L., Rorech, G.J., and Kidd, D.F., In-situ Treatment Technology, Second Edition, CRC Press LLC, 2001.
69. Agency for Toxic Substances and Disease Registry (ATSDR), "Toxicological Profile for N-Nitrosodimethylamine," December 1989.
70. U.S. EPA, "N-nitrosodimethylamine; CASRN 62-75-9 (04/01/97)," Integrated Risk Information Service (IRIS) Substance File, Internet download, 1997.
71. Bradley, P.M., Carr, S.A., Baird, R.B., and Chapelle, F.H., 2005, Biodegradation of N-nitrosodimethylamine in soil from a water reclamation facility: Bioremediation Journal, v. 9, no. 2, p. 115–120.
72. Westates Carbon, "Technical Bulletin #132, Aqua-Scrub Capacity Calculations Using Carbon Adsorption Isotherms for Toxic Organics," 1988.
73. Mitch, W.A., Sharp, J.O., Trussell, J.R., Valentine, R.L., Alvarez-Cohen, L., and Sedlak, D., "N-Nitrosodimethylamine (NDMA) as a Drinking Water Contaminant: A Review," Environmental Engineering Science, Volume 20, Number 5, 2003.
74. Solarchem Environmental Systems, "The UV/Oxidation Handbook," 1994.
75. U.S. EPA, "Proven Alternatives for Aboveground Treatment or Arsenic in Groundwater," October 2002.
76. U.S. EPA, "Arsenic Treatment Technologies for Soil, Waste, and Water," September 2002.
77. U.S. EPA, "Technologies and Costs for Removal of Arsenic from Drinking Water," December 2000.
78. Tenny, R., Adams, J., "Ferric Salts Reduce Arsenic in Mine Effluent by Combining Chemical and Biological Treatment," Environmental Science & Engineering, January 2001.
79. ATSDR, "Toxicological Profile for Chromium," September 2000.
80. U.S. EPA, "In-situ Treatment of Soil and Groundwater Contaminated with Chromium, Technical Resource Guide," Center for Environmental Research Information, National Risk Management Research Laboratories, Office of Research and Development, October 2000.
81. Cushnie Jr., G.C., "Pollution Prevention and Control Technologies for Plating Operations," National Center for Manufacturing Sciences, 1994.
82. Sabatini, D.A., Knox, R.C., Tucker, E.E., Puls, R.W., "Innovative Measures for Subsurface Chromium Remediation: Source Zone, Concentrated Plume, and Dilute Plume," U.S. EPA, National Risk Management Research Laboratory, September 1997.
83. Bahowick, S., Dobie, D., Kumamoto, G., "Ion-Exchange Resin for Removing Hexavalent Chromium from Ground Water at Treatment Facility C: Data on Removal, Regeneration Efficiency, and Operation," Lawrence Livermore National Laboratory, 1997.
84. Chung, J., Rittmann, R.E., Wright, W.F., Bowman, R.H., "Simultaneous Bio-Reduction of Nitrate, Perchlorate, Selenate, Chromate, Arsenate, and

Dibromochloropropane Using a Hydrogen-Based Membrane Biofilm Reactor," Biodegradation, 18, 199–209, 2007.
85. U.S. EPA, "Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium (VI) Plumes in Ground Water," National Risk Management Research Laboratory, Office of Research and Development, July 1997.
86. Suthersan, S., Remediation Engineering: Design Concepts, CRC Press LLC, 1997.
87. NTP, 1,2,3-Trichloropropane, Report on Carcinogens, Eleventh Edition; U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, January 2005.
88. World Health Organization (WHO), "Concise International Chemical Assessment Document 56: 1,2,3-Trichloropropane," 2003.
89. ATSDR, "Toxicological Profile for 1,2,3-Trichloropropane," September 1992.
90. Stepek, J., "Draft Groundwater Information Sheet, 1,2,3-Trichloropropane (TCP)," (California) State Water Resources Control Board, June, 2003.
91. Bosma, T., Damborsky, J., Stucki, G., Janssen, D.B., "Biodegradation of 1,2,3-Trichloropropane through Directed Evolution and Heterologous Expression of a Haloalkane Dehalogenase Gene," Applied and Environmental Microbiology, pp. 3582–3587, American Society for Microbiology, July, 2002.
92. Bowman, R.H., "Reduction of Perchlorate and Nitrate in Groundwater Using a Hollow-Fiber Membrane Biofilm Reactor (MBfR)," Proceedings of the 2005 National Ground Water Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, May 2005.
93. Graham, J., personal conversation, August, 2007.
94. Collins, H., "Existing and Emerging Water Quality Treatment Technologies," California Public Utilities Commission, "Securing Clean and Affordable Water" Symposium, September, 2006.
95. Dombeck, G., Borg, C., "Multi-Contaminant Treatment for 1,2,3-Trichloropropane Destruction Using the HiPOx Reactor," Proceedings of the 2005 NGWA Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, National Ground Water Association Press, 2005.

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